DEINKING OF NEWSPRINT BY FLOTATION METHOD

Bimo Ariadi, B.Sc. (Hons.)

A thesis submitted in fulfilment of the

requirements for the degree of

Master of Science

at the University of Tasmania

Department of Chemistry

University of Tasmania

July, 1995

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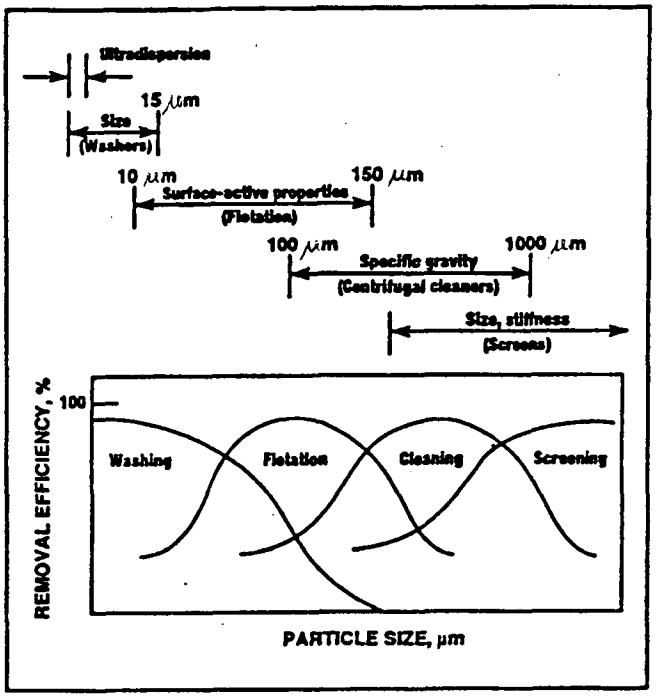

Figure 1.1. Optimum particle-size range for the various techniques in ink separation (after Shrinath et. al. [9])

1.2.2.1. Washing and flotation

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This thesis contains no material which has been accepted for the award of any other higher degree in any tertiary institution.

To the best of my knowledge, this thesis contains no material previously published, except where due reference is given in the text.

Bimo Ariadi

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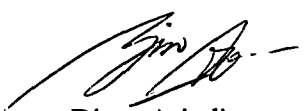

Bimo Ariadi

Abstract

There is much current interest in development of processes which lead to greater utilisation of secondary fibres in papermaking operations, both in Australia and overseas. The removal of ink from paper (deinking) is a major step in these processes. After repulping, ink can be removed from aqueous suspension by a number of techniques, one of which is flotation. Most commercial deinking facilities use flotation as the principle method of ink removal.

Studies have been made on the effects of flotation conditions, feedstock composition, and surfactant during flotation deinking of newspaper (ONP) and magazines (OMG). Type of surfactant and amount of surfactant appear to affect deinking performance. Temperature, pH, and furnish also appear to affect deinking efficiency of the various surfactants investigated. There is an optimum pH of 8.5 for flotation deinking of a 70/30 mixture of ONP/OMG using a fatty acid type deinking surfactant.

Increasing proportions of magazines (ash content of 26%) in the feedstock results in a deinked pulp with higher brightness. However, it was found that the higher brightness attained is largely due to the addition of higher brightness materials from the magazines, rather than a more efficient mechanism of ink removal from the ONP.

Addition of Ca^{2+} in the pulping stage at low level of addition seem to improve the brightness response for deinking of newspaper with fatty acids. High level of addition of Ca^{2+} seems to have detrimental effect.

An attempt is made to explain the results in terms of a model describing the flotation deinking process and the interactions occurring between surfactant molecules, ink particles, fibres, and air bubbles.

Acknowledgements

I would like to express my sincerest appreciation for the guidance and supervision provided by my supervisors Dr Lawrie Dunn, Dr Karen Stack and Associate Professor John Abbot throughout the entire course of this degree.

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Contents

Chapter 1

Deinking of Newsprint: An Overview

1.1. Introduction

Paper is one of the man-made substances that is universally used in everyday life, from newspapers, magazines, books, stationery, posters, tissue to packages, and many more. Predominantly, paper is produced from wood. However, over the last 100 years, recycled fibre has been an important source of paper making fibre, particularly for packaging grade paper. In response to current environmental issues, government legislation, and the market demands for paper containing recycled fibre, there is much current interest in development of processes which lead to greater utilisation of recycled fibres in paper-making operations both in Australia [1] and overseas. A large proportion of paper based material is recycled without the removal of ink. However, for paper grade requiring relatively high brightness, such as newsprint, the ink must be removed from the fibre and separated from the pulp stock. This process is known as deinking [2].

1.2. The principles of deinking

The deinking system consists of two characteristic steps. They are: (i) ink detachment from fibre and (ii) ink removal from stock.

1.2.1. Detachment of ink from fibre.

The first stage in the deinking process is referred to as pulping or repulping. Wastepaper pulping is a relatively simple process, being achieved by supplying water,

heat, chemicals, and mechanical energy. The main aims of repulping are to break down the wastepaper into discrete fibres and to separate the ink from the fibres [3].

Pulping is a critical operation in deinking because in this stage ink is removed from the fibre. Removal of ink particles from the fibre stock suspension is possible only if the ink particles are entirely detached from the fibres prior to entry into the separation stage.

Chemicals are normally added to the pulper just prior to the addition of furnish. Stock consistencies are usually between 4 and 6%; however there is a trend towards higher consistency (12-15%) pulping because of the savings in chemicals, heat, and other operational costs [4]. High alkalinity and temperature (50°C) are beneficial [5].

The amount of mechanical energy generated by the pulper is important in determining the rate of defibering and the rate of ink removal and dispersion. This mechanical energy is dependent upon the pulper configuration and the pulping consistency. However, the chemicals added to the pulper are the primary determinant of the level of ink dispersion and will be discussed later.

1.2.2. Ink removal from stock

After the ink is detached from the fibre, it must be removed from the stock. This is accomplished by a number of techniques, such as screening, cleaning, washing, and flotation. The size of the ink particles to be removed is the primary basis for choosing the appropriate technique.

Screens and centrifugal cleaners are used to remove large particles of ink. Particle size and shape do have some influence on ink removal by centrifugal cleaners, with larger particles (100-1000μm) being more effectively removed [6,7]. Ink removal by screening is poor because the flat ink particles tend to align themselves with the fibres and pass through the screen [8].

Flotation removes particles that are too small to be removed by screens and cleaners and yet are too big to be removed by washing. Washing is most efficient at removing the smallest particles of ink. The optimum size range for the different techniques is illustrated in Figure 1.1.

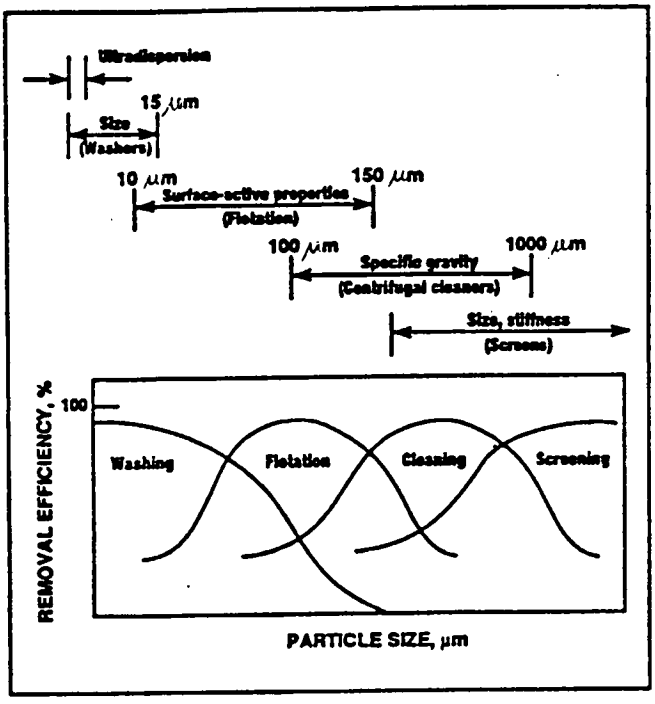


Figure 1.1. Optimum particle-size range for the various techniques in ink separation (after Shrinath et. al. [9])

1.2.2.1. Washing and flotation

In contrast to screening and cleaning, which are merely physical separation processes, washing and flotation operations require chemicals to help them perform efficiently.

Although washing and flotation are both carried out to remove ink particles, their operating principles are entirely different. Washing systems are most efficient at removing ink particles smaller than 10μm, while flotation works best at removing particles in the 10-100μm range. Furthermore, the washing process requires ink particles to remain in the aqueous phase so that they can be removed along with the

water. In contrast, flotation relies on the capture of ink particles by air bubbles, which rise to the surface, forming a foam that can be skimmed off as rejects. Ink particles separated by flotation must be rendered hydrophobic so that they can be easily separated from the water phase and attach themselves to air bubbles. Figure 1.2 depicts the mechanism involved in washing and flotation, which use different chemicals to accomplish their objectives.

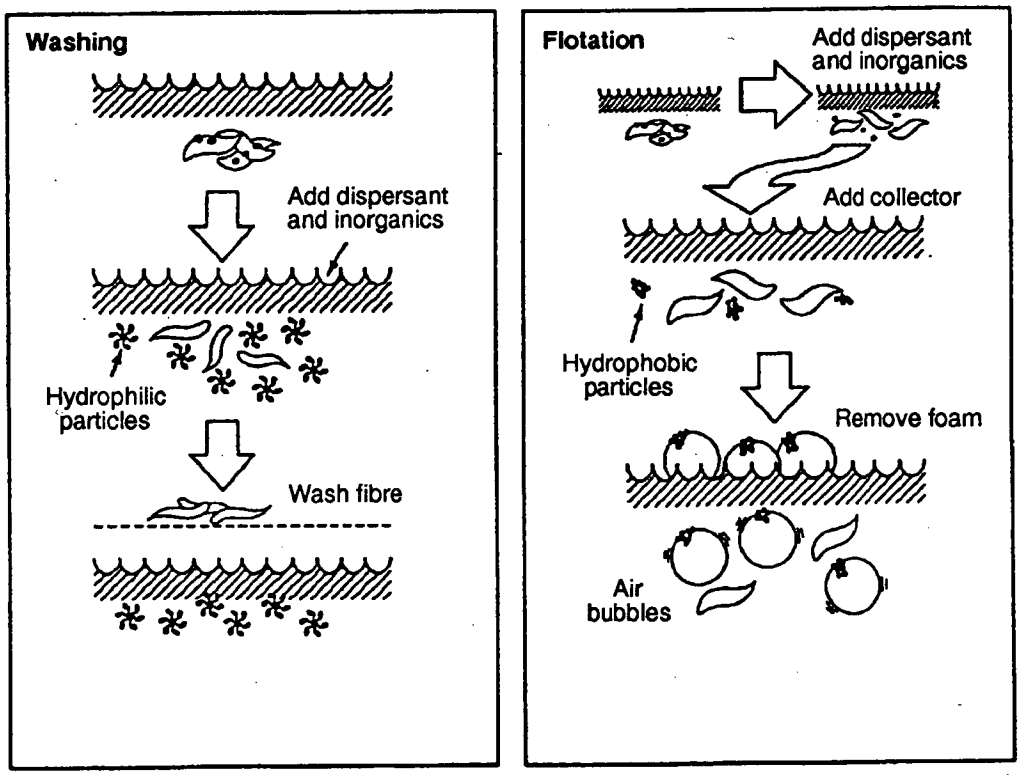


Figure 1.2. Comparison of washing and flotation (after Horacek and Jarrehult [10])

In washing, it is necessary to keep the ink particles finely dispersed and prevent their agglomeration [11]. To achieve this, dispersants are used. Washing also requires the ink particles to be rendered hydrophilic so they remain in the aqueous phase.

For flotation to be effective, the size of the ink particles must be maintained within the optimum range. The particles also must be hydrophobic. Particles that are

too small are not efficiently collected because of the low probability of encountering air bubbles. Very large particles are likely to be too bulky to be successfully carried to the surface by the bubbles. Hydrophobic particles are more easily separated from the aqueous phase and carried to the surface by air bubbles.

Table 1.1. illustrates the main differences of washing and flotation deinking. One implication of this comparison is that flotation is preferable for printing papers since fines and fillers are acceptable, but for products such as tissue, washing may offer some advantages [12].

Table 1.1. Comparison of washing and flotation (after Sauzedde [12])

	Flotation	Washing
Yield loss	5 - 10%	15 - 20%
Fillers and fines	Retained	Removed
Ink removed	Conc. sludge	Very dilute
Waste water	Some *in situ* treatment	Must be done externally
Chemical costs	Slightly lower	-
Capital costs	-	Somewhat lower
Pulp quality	Higher opacity	Higher strength

To take advantage of the benefits of both technologies, most new deinking plants will be a combination washing/flotation system. However, because of the conflicting operating principles of washing and flotation, chemicals that aid one process can hinder the other.

1.3. Printing inks

Since deinking deals with ink removal, it is essential to understand a little about printing inks. This section will discuss printing inks, especially those that are commonly used in newspaper and magazines.

Printing ink has two basic ingredients which are:

(i) Pigments, which provide the proper contrast to the image area and provide colour and opacity to the ink.

(ii) Vehicle, which carries the pigments and helps transfer the pigment to the sheet and aids in binding it there. Vehicles are generally vegetable oils, mineral distillates, and resins (natural and synthetic).

Printing inks also can contain several other components including binders, solvents, dryers, wetting agents, and waxes. The make up of the ink is determined by the type of paper on which it is to be applied, the method of application (printing process), the drying process, and the end use of the paper.

1.3.1. Types of inks

Ink is frequently classified according to its setting method. The general ink-setting methods (listed in Table 1.2) are absorption, evaporation, oxidation, and radiation curing [13, 14].

The absorption method is used with inks containing oil in the vehicle. The oil is absorbed by pores in the paper, leaving the pigment behind on the paper surface. This method is usually used in newsprint.

The evaporation method is used with inks containing volatile solvent vehicles that evaporate and cause the ink to dry. Vehicles are typically rosin esters or metal resinate binders dissolved in a suitable solvent. This method is used in letterpress and web offset printing for magazines and catalogues and in rotogravure printing of newspaper supplements.

The oxidation method is a combination of absorption and polymerisation of the oil or resin in the vehicle. The result is a polymerised film that is more flexible and tougher than films formed by the evaporation method. Both web and sheet fed offset printing processes use this technique.

The radiation curing method involves application of radiation to polymerise the ink. Radiation curing is used in high-gloss protective coating magazines and specialty products.

Table 1.2. Ink-setting method (after Scarlett [13] and Bassemir [14])

Ink-setting method	Vehicle composition	Ease of ink removal
Absorption	• Hydrocarbon (mineral) • Hydrocarbon resins	• Not subject to saponification • Vehicle must be emulsified and/or mechanically dispersed
Evaporation	• Hydrocarbon solvent • Rosin esters or metal resinate • Hydrocarbon resins • Alkyd resins and oleoresinous varnishes	• Rosin esters difficult to saponify • Metallic resinates saponifiable • Hydrocarbon resins need to be emulsified and/or dispersed
Oxidation	• High boiling hydrocarbons • Oil-modified alkyds • Oleoresinous varnishes • Phenolic-modified rosin esters	• Polymerised films not soluble in common solvents • Partially saponified with strong alkali at elevated temperature
Radiation curing	• Epoxy acrylates • Polyol acrylates • Urethane acrylates • Photo initiators - (aryl ketones)	• Not saponifiable • Chemical dispersion difficult • Not soluble in common solvents

1.4. The chemistry of deinking

1.4.1. Flotation Chemistry

The removal of ink particles by flotation is a physical-chemical process. It is based on the phenomenon that separation is achieved by influencing the wettability, with water, of the particles to be separated. The water-repellency of the surface of the particles to be separated is achieved by addition of special hetero-polar chemicals which deposit on the surface of the particles.

The course of the entire flotation process can be influenced by the variation of physical and chemical factors. Physical variables include the ink particle size and density, the size of the air bubbles, the consistency and temperature of the pulp slurry or suspension, as well as the velocity and flow conditions in the flotation cell. Among the chemical variables are the quality of the water (eg., water hardness), the pH value of the pulp slurry or suspension, and the flotation agents, such as collector and frothers.

Soaps, the alkali salts of fatty acids, with a long chain of molecules containing a hydrophobic (fatty acid) group at one end and a hydrophilic (functional) group at the other (Figure 1.3) are the best known collectors in flotation deinking [15].

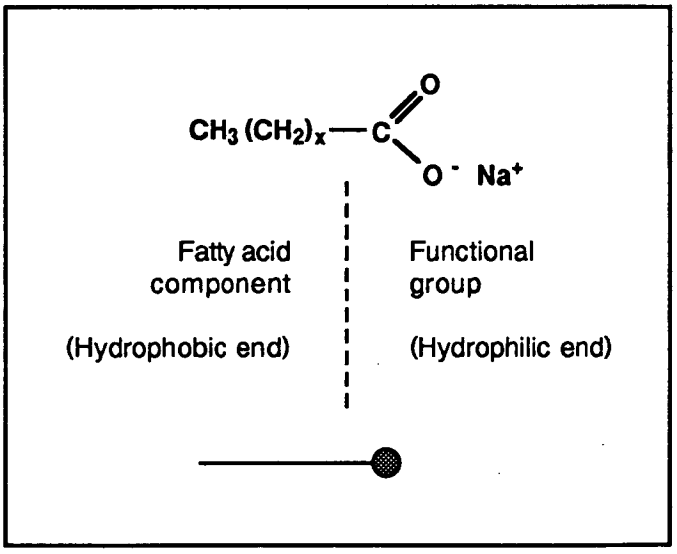


Figure 1.3. Example for a surface-active substance (soap)

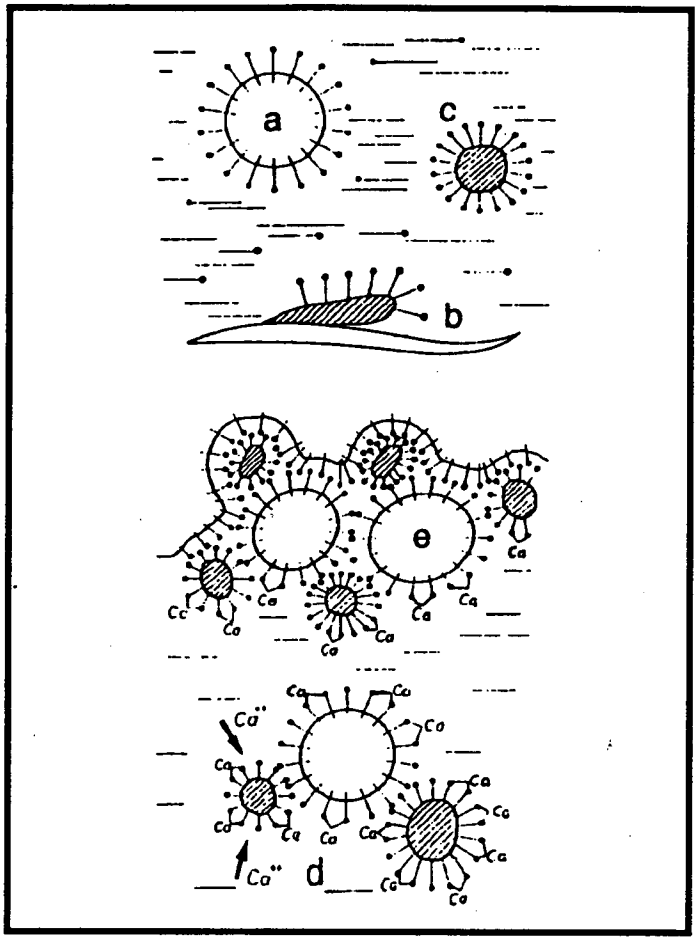
The simplified reaction mechanism of ink flotation proposed by Ortner et.al.[16] is shown in Figure 1.4. The surface-active substances, which reduce surface tension, lead to the formation of froth on the water-air boundary. The hydrophobic ends face the ink particles, and the hydrophilic ends are directed towards the water. As a result, the enveloped ink particles appear hydrophilic on the outside and detach more easily from the fibre(1.4b). To deposit the dispersed ink particles (1.4c) on air bubbles (1.4a), the hydrophilic ends of the soap molecules must react with hardening constituents of water (eg., Ca^{2+}) so that they act as collectors (1.4d). The soaps precipitated by the hardening constituents of the water act as collectors, while the non-precipitated soaps are effective as frothers and dispersing agents.

1.4.2. Chemical reaction/mechanism in deinking

In flotation deinking, prior to flotation stage, it is very important that ink is sufficiently broken up and dispersed in the pulper. Chemicals are added to enhance this process. The addition of chemicals causes a number of complex reactions to occur. Some of the general reactions and mechanisms involved will be discussed.

1.4.2.1. Fibre Swelling

This process begins as soon as the wastepaper is immersed in water. The water molecules form hydrogen bonds with the cellulose molecules and break interfibre hydrogen bonds. The effect is enhanced with the addition of caustic and elevated temperature [17]. The breaking of interfibre bonds and swelling of fibres are an important part in deinking, as they greatly facilitate loosening and removal of ink particles and coatings from fibre surfaces.


a
c
b
e
Ca
Ca
Ca

Many of the resins used as ink binders are esters and therefore can be broken up in hot alkali solutions. This is one of the principle reactions occurring in high pH deinking of conventional offset and gravure inks. The oily vehicle in standard newsprint ink is similar to hydrocarbons; therefore, it is not subject to saponification. This is also the case for the modified hydrocarbon resins often used in offset inks. Phenolic modified rosin esters can be saponified under severe conditions of pH and temperatures.

1.4.2.3. Wetting

This is a surface or interfacial phenomenon that plays a key role in pulping liquor penetration into the fibre network. When a liquid surface is in contact with a solid, the molecules at the interface may be more attracted to the solid than to the bulk liquid. If so, the molecules tend to spread out over the solid and the surface area of the liquid is increased. This phenomenon is called wetting. Proper wetting allows more rapid penetration of chemicals into the fibre network and inter-fibre contact area and helps inks break up and separate from fibres.

1.4.2.4. Emulsification/Solubilisation

Emulsification is the dispersion of one liquid phase into another to form a significantly stable suspension. Similar to wetting, emulsification is a surface phenomenon that requires addition of surfactants to alter the interfacial tension between the phases. Emulsification is an important chemical mechanism in deinking only when there are oils present in the ink. These inks are used in letterpress and offset printing of newspaper and magazines, and they dry primarily by absorption. Adsorption of emulsifying agents (surfactants) at the oil/fibre interface releases the oil from the fibre (with the pigment particles) and forms an oil in water emulsion.

Solubilisation is the dissolving of substances in a medium in which they are normally insoluble. Solubilisation differs from emulsification in that in the former the

solubilised material is in the same phase as the solution while the latter is a dispersion. Solubilisation may be the most important mechanism for the removal of oily inks, as it has been observed [18] that removal of oily soil from textile surfaces becomes significant only under conditions that favour solubilisation.

1.4.2.5. Sequestration/Precipitation

The presence of polyvalent cations - notably calcium, magnesium, and iron - can be detrimental to the deinking process even, to a certain extent, when nonionic surfactants are used. These cations can reduce negative surface charges on both fibre and ink [19] leading to agglomeration and redeposition, and cations also may act as linkages between negatively-charged fibres and negatively-charged ink particles. These ions enter the system in the water or paper stock and can be removed by sequestration (formation of a water-soluble complex) and precipitation (formation of an insoluble precipitate).

1.4.2.6. Anti-redeposition

Anti-redeposition refers to the prevention of suspended particles from precipitating onto the substrate from which they were removed. In deinking, the dispersed ink particles must be kept from settling back onto the fibres. Anti-redeposition is achieved by sterically inhibiting the approach of ink particles to fibres.

1.5. Deinking chemicals

Chemicals for deinking are chosen based on wastepaper, ink types, and design of the deinking system (washing or flotation). Also of importance is the quality of stock going to the paper machine. Many mills are incorporating various percentages of deinked fibre into their final product. The amount of deinked stock that may be blended with virgin fibre is largely determined by the quality of the deinked stock. For a specific deinking system that quality may be controlled by careful use of

deinking chemicals. The following sections will discuss common deinking chemicals in some detail.

1.5.1. Sodium hydroxide

Sodium hydroxide (NaOH), also referred to as caustic soda, is one of the most important deinking chemicals for wood-free secondary fibre, as well as for deinking wood-containing furnishes such as newsprint. High concentrations of alkali can saponify and/or hydrolise many ink binders and will swell fibres, aiding in the breaking up of inks and coatings.

However, addition of sodium hydroxide to wood-containing furnishes will cause the pulp to yellow and darken. This is a phenomenon often referred to as alkali darkening. It was reported that the effect of pH on the formation of chromophores in lignin increase as the pH rises above 5.5 [20].

1.5.2. Hydrogen peroxide

Hydrogen peroxide (H_2O_2) is used to decolourise the chromophores generated by the alkaline pH in a wood-containing furnish. The peroxide reaction with sodium hydroxide is as follows:

$$H_2O_2 + NaOH \longrightarrow HOO^- + H_2O$$

The bleaching action of hydrogen peroxide is attributed to the oxidative action of the perhydroxyl anion (HOO^-) [21,22]. To maximise the amount of perhydroxyl anion (HOO^-) peroxide bleaching is normally carried out under alkaline conditions. However, it is also well known that hydrogen peroxide has a tendency to decompose according to the following equation:

$$H_2O_2 \longrightarrow {}^1/_2\, O_2 + H_2O$$

which is known to be catalysed by the presence of heavy metal ions like manganese, copper, and iron, high pH and temperature [23,24,25].

Hydrogen peroxide decomposition can be reduced by addition of small amounts of the pentasodium salt of diethylenetriaminepentaacetic acid (Na_5DTPA) [23]. Sodium silicate is also an important additive in peroxide bleaching of mechanical pulps. Evidence indicates that silicate does not stabilise peroxide by itself but stabilises the environment within which the peroxide works [26].

1.5.3. Silicates

Silicates have been used since the turn of the century in deinking wastepaper. It was reported that silicates, compared to caustic soda alone, provide better ink removal and brighter pulps with less fibre damage [27].

Silicates are complex solutions of polymeric silicate anions which are surface active. This surface activity is what gives silicates many of their deinking functions, including emulsification and suspension of dispersed ink [28].

Sodium silicate is a good stabiliser for alkaline peroxide bleaching solutions. Silicates tend to decrease the rate of peroxide decomposition by inactivating heavy metal catalysts present in the bleaching solution [29,30,31]. Silicates are used primarily in deinking newsprint or other high groundwood containing furnishes.

1.5.4. Chelating agents

DTPA (diethylene triamine penta-acetic acid) is the most commonly used chelant. The role of chelant is to form soluble complexes with heavy metal ions [26]. The structure of DTPA is shown in Figure 1.5. The complexes prevent the heavy metal ions from decomposing the hydrogen peroxide. The metals can be sourced from the wastepaper or from the water. DTPA will chelate metals in the following order of

priority [32]:

$$Ni^{2+} > Cu^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Pb^{2+} >$$
$$Zn^{2+} > Fe^{3+} > Ca^{2+} > Mg^{2+} > Al^{3+}$$

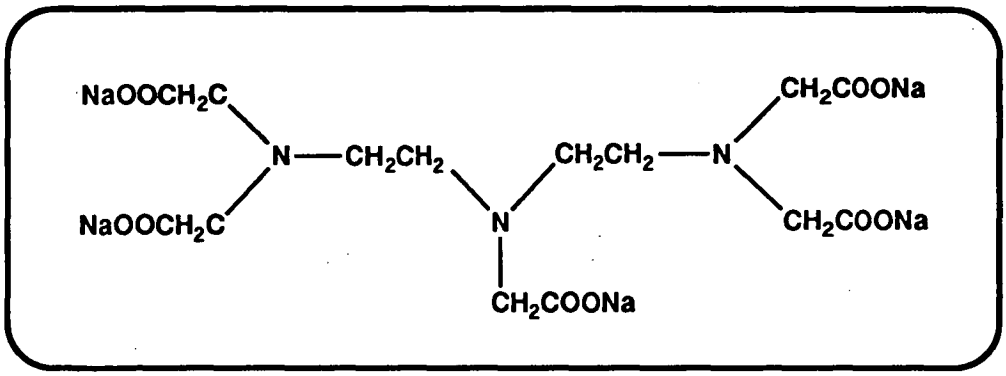


Figure 1.5. The structure for Na_5DTPA

1.5.5. Surfactants

Surfactants are surface active substances that contain an organic part that has an affinity for oils (hydrophobe) and another part that has an affinity for the water phase (hydrophile). The hydrophobic group is usually a long chain hydrocarbon residue while the hydrophilic group is ionic or, in the case of nonionic surfactants, a highly polar group. These surfactants function in deinking systems by lowering the surface tension of water to enable it to "wet" more effectively, adsorbing onto surfaces to aid in ink removal and dispersion, and by solubilisation and emulsification.

Surfactant chemistry and its practical application are complex. There are thousands of available surfactants whose function and performance are influenced by many application conditions. Blends of surfactants will provide better performance than single components [18].

Several surfactant properties play a significant role in determining surfactant effectiveness. They include surface tension and interfacial tension, critical micelle concentration (cmc), hydrophilic-lipophilic balance (HLB), and surfactant foaming.

1.5.5.1. Surface and interfacial tension

Interfacial tension is defined as the work required to increase the area of an interface isothermally and reversibly by a unit amount. In speaking of the liquid-air interface, it is general practice to use the term surface tension.

As has been mentioned before the surface-active molecules are characterised by the presence of a polar and a non-polar group. The polar portion of the molecule is surrounded by a strong electromagnetic field and exhibits a high affinity for other polar groups and molecules, including water. The non-polar portion of the molecule has a low affinity for water and other polar molecules. The surface energy of a liquid or a solution depends on the potential energy of the electromagnetic field which extends outwards from the surface layer atoms. For the surface energy, to have a minimum value, it is necessary that the molecules present in the solution arrange themselves so that the least active portions of the various species present in the solution are exposed at the surface [33]. Thus, for solutions of surfactants in water, the surfactants molecules will tend to concentrate at the surface, with the non-polar portion directed outwards (Figure 1.6). This arrangement provides the minimum contact between the water molecules and the non-polar hydrocarbon chain of the surfactant molecule, thereby reducing the solution surface tension.

Surface tension is an important concept in surfactant chemistry. It can be conceptualised as a force per unit length at a right angle to the force required to pull molecules apart to expand the surface area [18]. Therefore, a liquid with low surface tension spreads more.

1.5.5.2. Critical micelle concentration

The concentration of surfactant at which the concentration of micelles suddenly becomes appreciable is referred to as the critical micelle concentration (cmc). The surface activity, in general, is due to non-micellar surfactants and the micelles act as a reservoir for the unassociated surfactants molecules and ions. At a concentration

greater than the cmc value, the surface tension of the solution does not decrease further with an increase in surfactant concentration, since surfactant molecules are forming micelles in the bulk of the solution instead of packing the surface of the liquid (Figure 1.6).

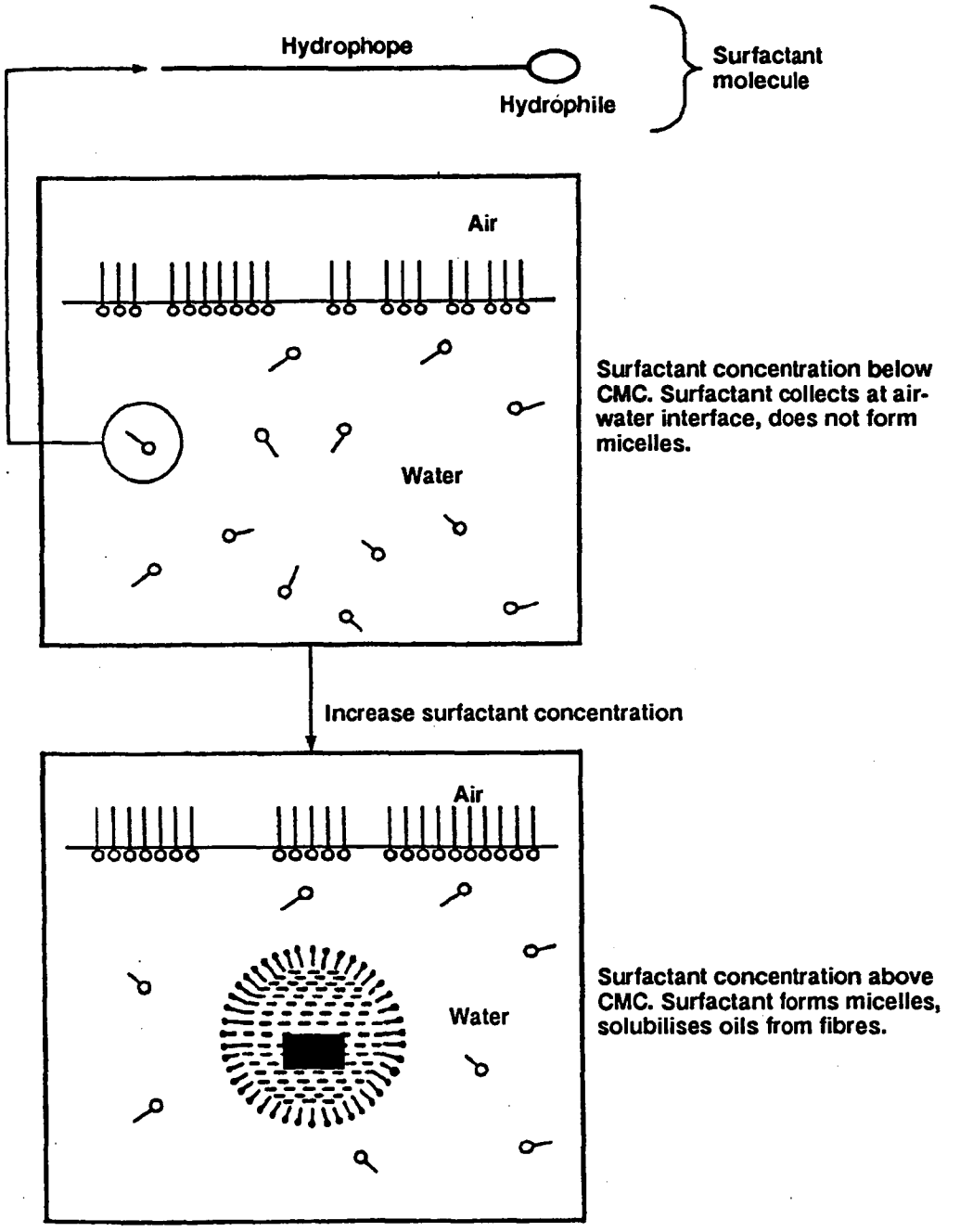


Figure 1.6. The schematic diagram of surfactants in solution (after Borchardt [34])

The ability of surfactant solutions to dissolve or solubilise water-insoluble materials, so as to remove ink from fibre, is due to the formation of micelles. Micelles are clusters of surfactant molecules in which the hydrophiles are oriented towards the water phase. The hydrophobes are oriented away from the aqueous phase and towards the interior of the micelle (Figure 1.6). This creates an oil-like environment in the interior of the micelle. Oils such as ink vehicles are solubilised when they are taken into the interior of surfactant micelles.

1.5.5.3. Hydrophilic-lipophilic balance

One way of characterising surfactants is by their hydrophilic-lipophilic balance or HLB. This concept was developed by Griffin [35,36] and is based on the fact that any surface active agent contains both hydrophilic and lipophilic groups, and the ratio of their respective weight percentages should influence their dispersive and emulsifying behaviour. A low HLB indicates a surfactant that is lipophilic in character, while a high HLB indicates one that is hydrophilic in character. Table 1.3 illustrates the application of surfactants as related to HLB value.

Table 1.3. Surfactant application as related to HLB value (after Griffin [35])

HLB value	Use
4 - 6	water in oil emulsifier
7 - 9	wetting agent
8 - 18	oil in water emulsifier
13 - 15	detergency
15 - 18	solubilising agent

Turai and Williams [37] have done some experiments on the role that HLB has on deinking efficiency. In their work, they found that in the deinking of newsprint the optimum HLB value for nonionic surfactant is in the range 14.5 to 15.5.

1.5.5.4. Surfactant foaming

The foaming process is depicted in Figure 1.7. Surfactant molecules orient themselves around an air bubble with the hydrophobe pointing towards the bubble and away from the aqueous pulp slurry. The surfactant hydrophile groups are oriented towards the aqueous phase. Since an air bubble is less dense than water, it rises to the top of the pulp slurry. If foam generation is faster than the rate that air bubbles break open, a foam layer builds up.

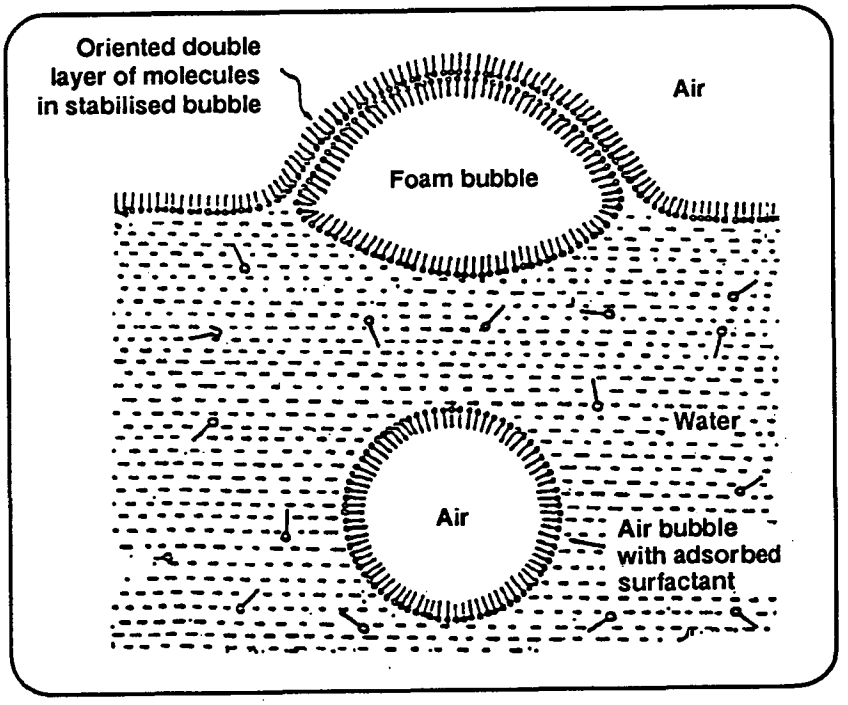


Figure 1.7. Surfactant stabilisation of air bubbles and foam formation (after Borchardt [34])

In flotation deinking, foaming separates the ink particles from the pulp slurry and traps them in a froth layer. Since, even below the cmc, some surfactant molecules congregate at the air-water interface (as indicated in Figure 1.6), foaming can occur

below the cmc. Thus, surfactants may be used in a flotation cell below the critical micelle concentration.

1.6. Objectives of the study

The main objectives of the study on the deinking of newsprint by flotation are to define the general principles for the behaviour of deinking chemicals, in particular the surfactants, under flotation deinking conditions and also to gain an understanding of the surface chemistry phenomena in the deinking of newsprint, particularly those that control the efficiency of deinking.

The study will investigate the effects of flotation conditions such as pH and temperature, feedstock composition, and surfactant during flotation deinking of newspaper (ONP) and magazines (OMG). The results of these experiments will be explained in terms of a model describing the flotation deinking process.

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Chapter 2

Experimental

2.1. Laboratory scale flotation deinking method

This section describes the method used for flotation deinking. The equipment used is a laboratory scale Lamort Deinking Unit (see Figure 2.1), which can be set up in the pulper (Figure 2.1.a) or flotation (Figure 2.1b) arrangement. This unit enables one to duplicate industrial operating conditions of a pulper or a deinking unit with relatively small quantities of waste paper.

2.1.1. Stock preparation and reagents

Old newspaper(ONP) was obtained in batches of recently printed offset Mercury newspaper (2-3 months old) from The Mercury Press in Hobart, while a range of magazines (OMG) was obtained, also in batches, from the Angus and Robertson Bookstore in Hobart. A selection of magazines (eg. Cleo, Women's Weekly etc.) was taken as representative of coated magazines. The age of these magazines was approximately 6-12 months.

Different batches of ONP and OMG were used for the experiments during the course of this study. Brightness from different batches of ONP and OMG varied slightly (by 1 - 2 unit).

The newspaper and magazines were separately torn into 2-3 cm squares. All staples and glue from bindings were removed prior to pulping, and the samples were stored in opaque plastic bags.

Sodium hydroxide (98%) and hydrogen peroxide (30%) were obtained from BDH chemicals. DTPA (97%) and fatty acids were obtained from Aldrich. Sodium

silicate (30%) was provided by Aluminates Chemicals, Burnie, Tasmania. The deinking surfactant samples, designated as surfactants A, B, C, and D, were supplied by Buckman Laboratories.

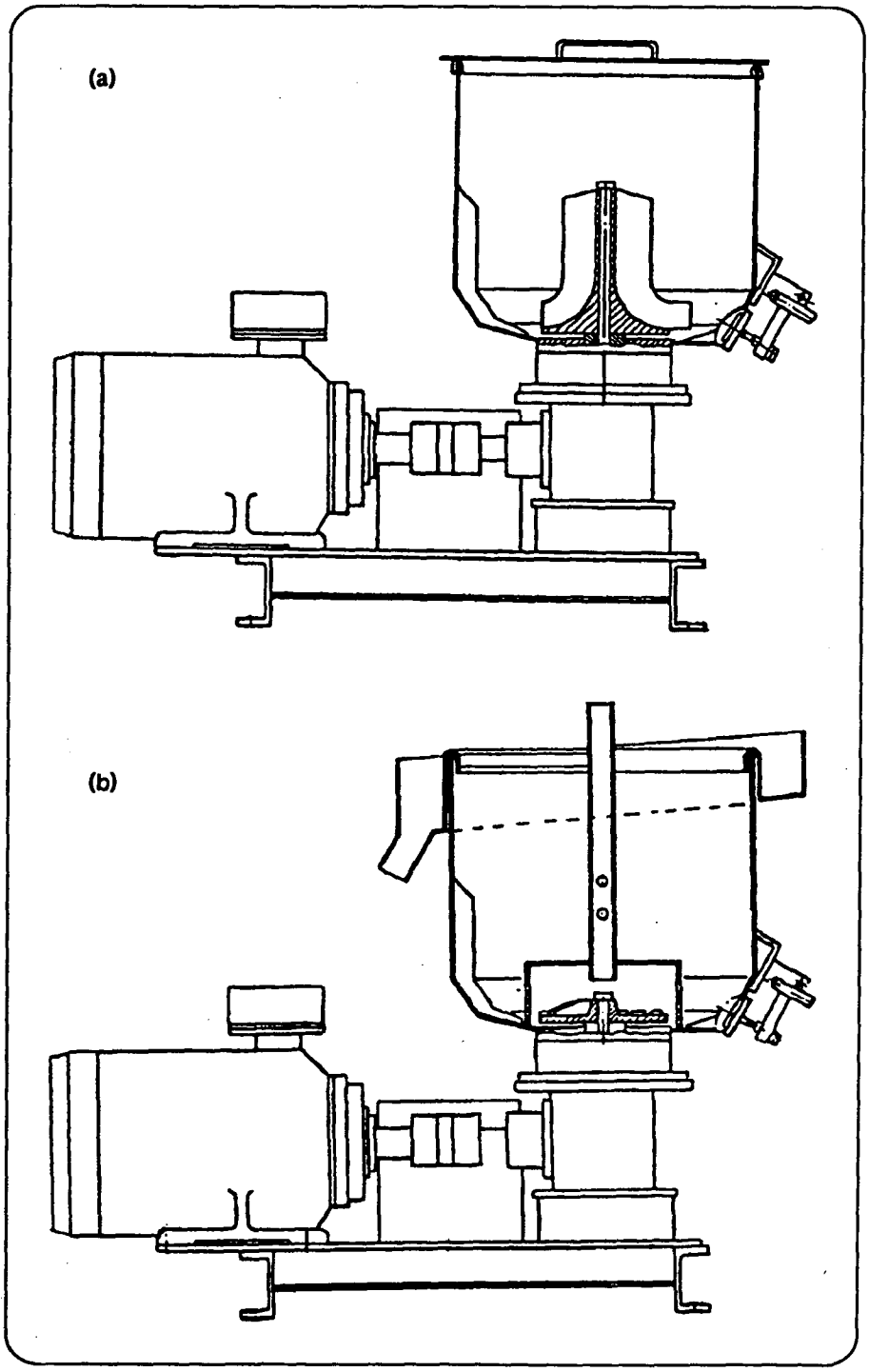

Figure 2.1. Schematic diagram of Lamort Deinking Unit in (a) pulper and (b) flotation arrangement.

2.1.2. Pulping

In the pulping stage the Helico Pulper was installed into the Lamort deinking unit. Pulping was carried out using 750g o.d. fibre at 8% consistency. Hot water at 50°C and chemicals (1% NaOH, 1% sodium silicate, 1% H_2O_2, 0.2% DTPA, and 0.4% deinking surfactants) were introduced into the pulper before the waste paper. Once a good rolling/mixing action was achieved, pulping was continued for 20 minutes.

2.1.3. Flotation

For flotation, the Lamort Hyperflotation Kit replaced the Helico Rotor, incorporating an aeration screen and air suction column on the rotor and installing an overflow weir for ink sludge collection. A 450 g o.d. sample of the repulped stock was used for flotation. The stock was diluted with water to fill up the tank. In some instances the rotor was also used as a mixer for adjusting the pH of the slurry, before putting the aeration screen in place. Flotation was performed at a consistency of 1% and temperature of 50°C. The temperature and pH of the pulp slurry in the tank remained quite stable during the flotation.

2.2. Measurement of brightness and colour

2.2.1. Handsheet preparation.

Handsheets were formed to evaluate the repulped and post-flotation (deinked) stock. The stock was acidified to pH 5 prior to sheet formation, to simulate the pH shock deinked pulp would experience prior to being used in acidic paper-making conditions. The method used in preparing the handsheet is similar to that described in TAPPI Official Methods (T218 om-91) [1] using No. 41 filter paper. The filter paper was removed before drying. Three handsheets were prepared for each experiment.

2.2.2. Brightness measurement

The term brightness refers to the reflection of light at a wavelength of 457 nm. This particular wavelength measurement gives good correlation with what the eye appreciates as brightness. Brightness readings were made using an Elrepho 2000 Spectrophotometer (Figure 2.2) at 457nm. Measurements were taken on both sides of the sheets and reported as an average.

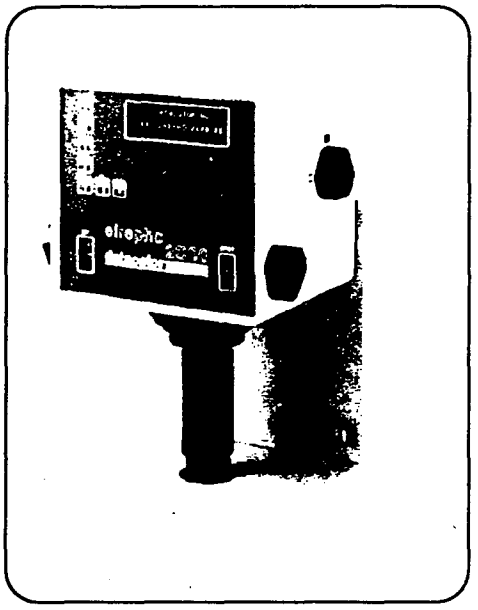

Figure 2.2. The Elrepho 2000 spectrophotometer.

2.2.3. Measurement of colour by L*, a*, b* system

The L*, a*, b* system locates the colour in a colour solid. The diagram for the L*, a*, b* system is given in Figure 2.3. The L* coordinate represents the lightness from black at the bottom through a series of greys to white at the top. The a* coordinate goes from green to red and the b* coordinate from blue to yellow. The L*, a*, b* colour scales are expressed in National Bureau of Standards units of colour difference. The magnitude of this unit is such that one unit represents about the maximum colour difference that an observer will tolerate in an average commercial

colour match. The L*, a*, b* values were also measured using the Elrepho 2000 Spectrophotometer.

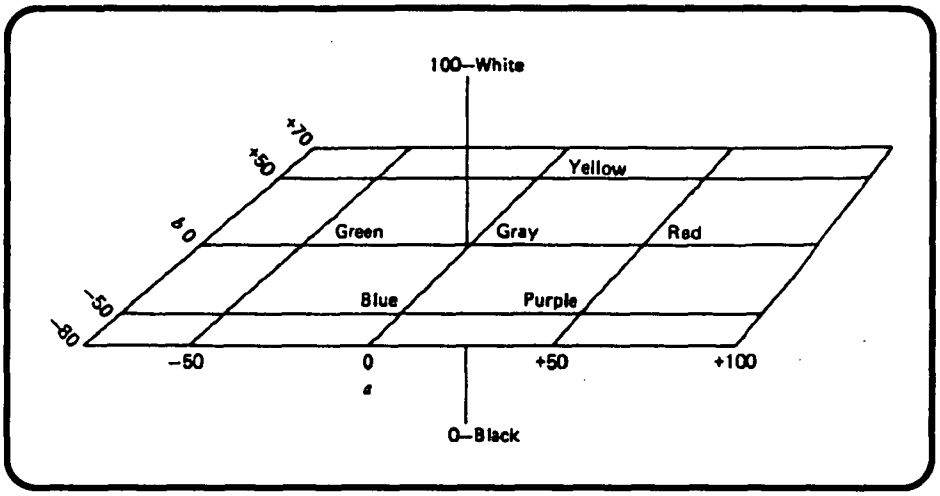

Figure 2.3. Rectangular dimensions of the L*, a*, b* solid for designating the colours of surfaces (after Casey [2]).

2.3. Speck count analysis

A speck count of the handsheet made from deinked pulp was made using an image analysis facility at Australian Newsprint Mills Research Division at Boyer, Tasmania [3]. The equipment for image analysis consisted of an IBM PC/XT computer, two display monitors and a Panasonic video camera. Used in conjunction with this are a Pentax macro lens and a light source consisting of two incandescent globes. The basic image analysis software consists of a package called Visilog.

The image analysis equipment detects ink particles which are greater than 65 μm and its measurement area is 512 x 512 pixel (where 1 pixel is equal to 65 μm). The image analysis equipment was calibrated with a grey tile which has an ISO brightness of 53%. In speck count analysis, any specks in the handsheet which are darker than 53% brightness were detected by the image analysis software and the area of the specks calculated in parts per million or mm^2 of specks per m^2 of handsheet.

2.4. Measurement of surface tension

Surface tension measurements were made using an Analite surface tension meter (Figure 2.4). The surface tension meter consists of a movable platform which is raised or lowered by means of a fine height control mechanism, a thin glass plate and a plate holder. These components are located in a working area which is enclosed by sliding glass doors to prevent draughts and reduce sample contamination.

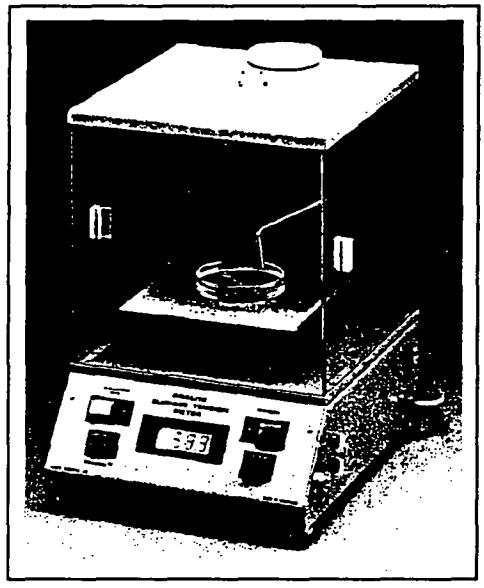

Figure 2.4. Analite Surface Tension Meter.

For measuring surface tension, the fluid sample to be measured is placed in a container on the platform, and the platform is raised until the glass plate is fractionally immersed in the fluid. The surface tension is indicated directly on the digital readout in millinewtons per meter when using the standard glass plates which are supplied with the meter.

2.5. Measurement of water hardness

Water hardness measurements were made using a Univer Water Hardness Kit, which consists of EDTA titrant (0.35N), Univer hardness reagent powder

pillows, plastic measuring tube (5.83 mL) and square mixing bottle. For measuring water hardness, one full measuring tube of water sample to be measured was transferred to a square mixing bottle and mixed with the contents of one Univer hardness reagent powder pillow. The mixture then was titrated against EDTA until the colour changes from red to blue. The water hardness of the sample was expressed in mg/L of hardness as calcium carbonate ($CaCO_3$).

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Chapter 3

Conditions in Flotation Deinking

3.1. Introduction

Alkalinity is known to affect the peroxide bleaching reaction. Alkaline chemicals react with hydrogen peroxide to form the perhydroxyl ion, HOO^-, which is instrumental in the bleaching action of the hydrogen peroxide [1,2]

$$H_2O_2 + OH^- \longrightarrow H_2O + HOO^-$$

However, it is also widely known that high alkalinity in wood-containing feedstock will cause the pulp to yellow and darken. It was shown that the formation of chromophores in lignin rapidly increase as the pH rises above 5.5 [1]. This is a phenomenon often referred to as alkali darkening.

Sodium hydroxide (NaOH), also referred to as caustic soda, is used in deinking formulation to adjust the pH to the alkaline region, pH 9.5 - 11, conventionally employed in pulping [3]. The presence of alkali causes the fibre to swell and opens up fibrils, thus helping the detachment of ink particles from the fibres. Alkali partially breaks down vegetable oil ink vehicles by saponification and controls chemical species in solution (such as DTPA) by pH. Hence, it is important to know the effects of alkalinity in flotation deinking. This chapter aims to investigate the effects of NaOH addition and flotation pH on efficiency of deinking as measured by brightness at 457nm, and colour using the L*, a*, b* scales. The effects of temperature will also be discussed.

The experiments that were carried out in investigating the effects of alkalinity and temperature employed several different surfactants as listed in Table 3.1.

Table 3.1. Type of deinking surfactants used (supplied by Buckman Laboratories)

Surfactant sample	Main Components
A	Combination of fatty acids and a non-ionic surfactant.
B	Combination of fatty acid soaps, a non-ionic surfactant, and ethylene glycol.
C	Combination of dimethylamide of C_{18} oil, non-ionic surfactant, anionic surfactant, dipropylene glycol methyl ether, and aromatic solvent.

3.2. Effects of NaOH addition and flotation pH

3.2.1. Effects of varying NaOH addition in pulping stage

Caustic soda (NaOH) is one of the main ingredients in deinking formulation. The addition rate of NaOH in industry is usually stated in terms of percentage on ovendry fibre. The following experiments were done to investigate the effects of varying the initial amount of NaOH applied at the pulping stage, keeping other variables at constant values. The deinking feedstock that is used is the 70/30 mixture of offset printed newspaper and coated magazines. This feedstock composition is chosen because it is the composition that is generally accepted as a desirable feedstock for the deinking process in industry, as both are available in large quantities.

The efficiency of deinking is measured in terms of brightness at 457 nm as well as colour in the L*, a*, b* scales, as some researchers [4] have stated that colour measurements made with the L*, a*, b* colour scale are preferable to brightness measurements made at 457 nm as a means of accurately representing ink removal.

Figures 3.1 to 3.4 present the results of the effect of varying the initial amount of NaOH applied at the pulping stage on deinking of 70/30 mixture of offset printed newspaper and coated magazines by using the deinking surfactant A, which is predominantly a mixture of saturated and unsaturated fatty acid soaps.

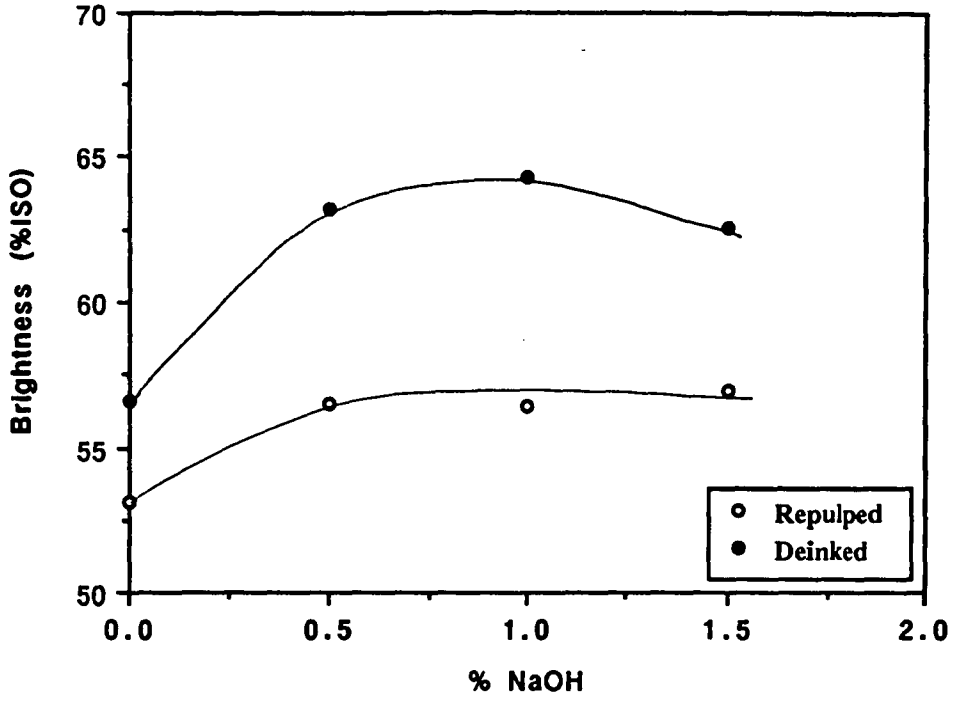

Figure 3.1. Effect of NaOH addition (as % o.d. fibre) on brightness of pulp after pulping and flotation for deinking of 70/30 mixture of ONP/OMG using surfactant A. Pulping conditions: 1% H_2O_2, 1% sodium silicate, 0.2% DTPA, 0.4% surfactant A; time 20 mins; temperature 50°C; consistency 8%. Flotation conditions: time 6 mins; temperature 50°C; consistency 1%.

Figure 3.1 shows an increase in brightness after pulping with increasing %NaOH applied (indicated by empty dots). It also illustrates that there seems to be an optimum %NaOH (or more likely pH) for the brightness after flotation (indicated by filled dots). The apparent decrease above 1% NaOH for the brightness after flotation is probably due to alkali darkening. The decrease in brightness after pulping above 1% NaOH is not apparent, probably due to the existence of perhydroxyl ion at sufficient concentration to counter the yellowing or chromophore creation due to high alkalinity. At the flotation stage, the pulp consistency is diluted to 1% consistency, hence the concentration of perhydroxyl ion in terms of molarity is also reduced by approximately a factor of 8. Meanwhile, pH of the pulp slurry remains high at pH > 9.5 (Table 3.2).

Table 3.2. The correspondent pH values associated with the initial amount of NaOH applied.

Initial NaOH (% on o.d. fibre)	pH after pulping	initial flotation pH
0.0	7.8	7.5
0.5	9.5	9.0
1.0	10	9.5
2.0	10.5	10.0

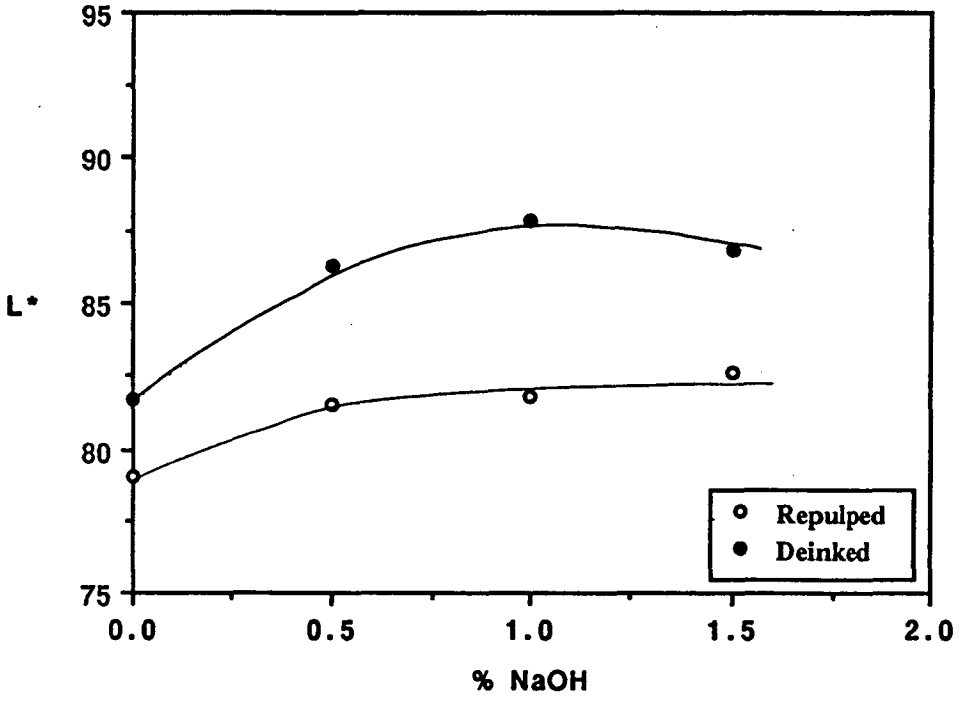

Figure 3.2. Effect of NaOH addition (as % o.d. fibre) on L* of pulp after pulping and flotation for deinking of 70/30 mixture of ONP/OMG using surfactant A. Pulping and flotation conditions as in Figure 3.1.

The L* values (in Figure 3.2), which are a measure of greyness, show similar trends to the brightness measurements at 457 nm (Figure 3.1). It shows increasing L* values after pulping with increasing %NaOH applied, with diminishing rate of increase as %NaOH increased.

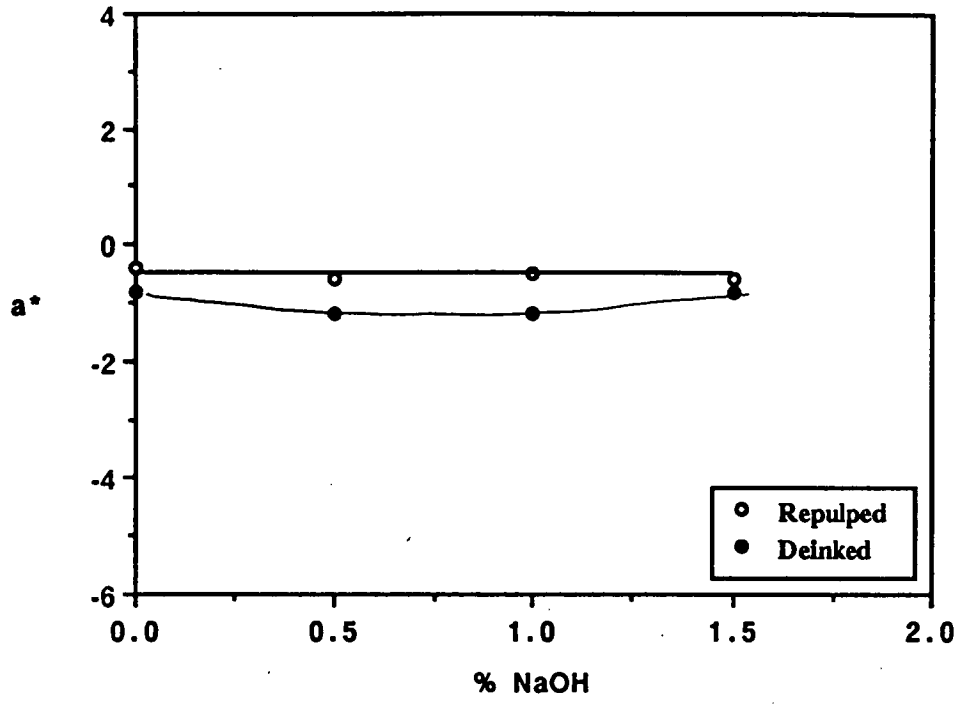

Figure 3.3. Effect of NaOH addition (as % o.d. fibre) on a* of pulp after pulping and flotation for deinking of 70/30 mixture of ONP/OMG using surfactant A. Pulping and flotation conditions as in Figure 3.1.

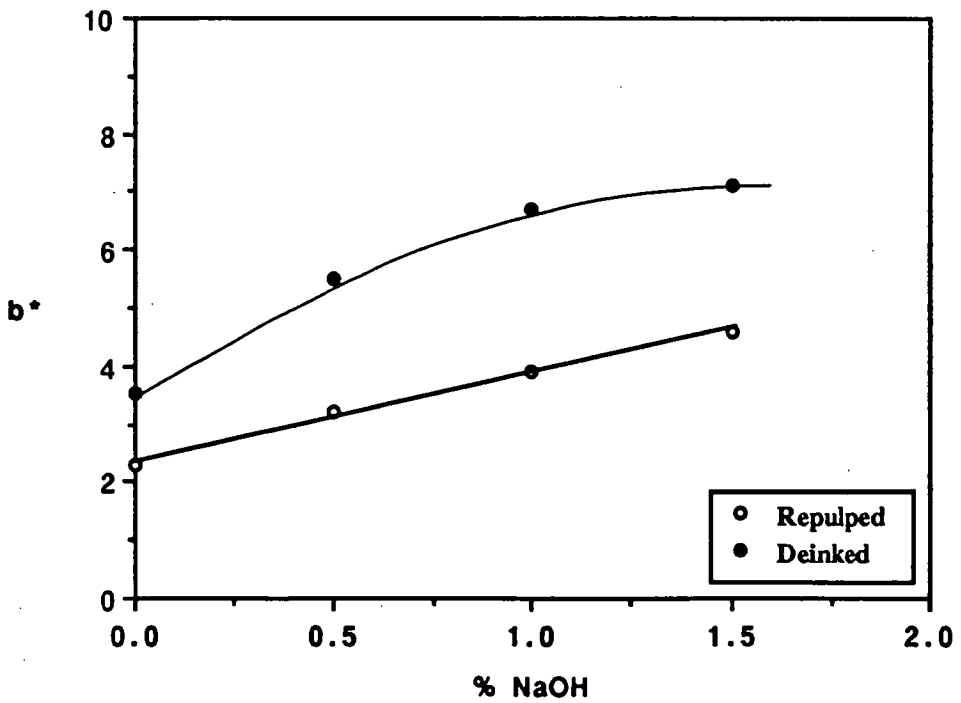

Figure 3.4. Effect of NaOH addition (as % o.d. fibre) on b* of pulp after pulping and flotation for deinking of 70/30 mixture of ONP/OMG using surfactant A. Pulping and flotation conditions as in Figure 3.1.

There seems to be very little change in a* values, which are an indication of the green-red tint of paper, with change in %NaOH after pulping. The value of a* remains constant at -0.6 after pulping (Figure 3.3).

Figure 3.4 shows that, after pulping, b* values, which are an indication of the yellowness of the paper, increase with %NaOH. It is apparent that b* values after flotation are higher than those after pulping, indicating that the yellowing reaction is occurring further in the flotation stage, where it is favoured by the high alkalinity and low concentration of perhydroxyl ion present in the flotation stage.

Figures 3.5 to 3.8 present the results of the effect of varying the initial amount of NaOH applied at the pulping stage on deinking of 70/30 mixture of offset printed newspaper and coated magazines by using the deinking surfactant C, which is predominantly a mixture of saturated and unsaturated dimethylamides of a C_{18} oil.

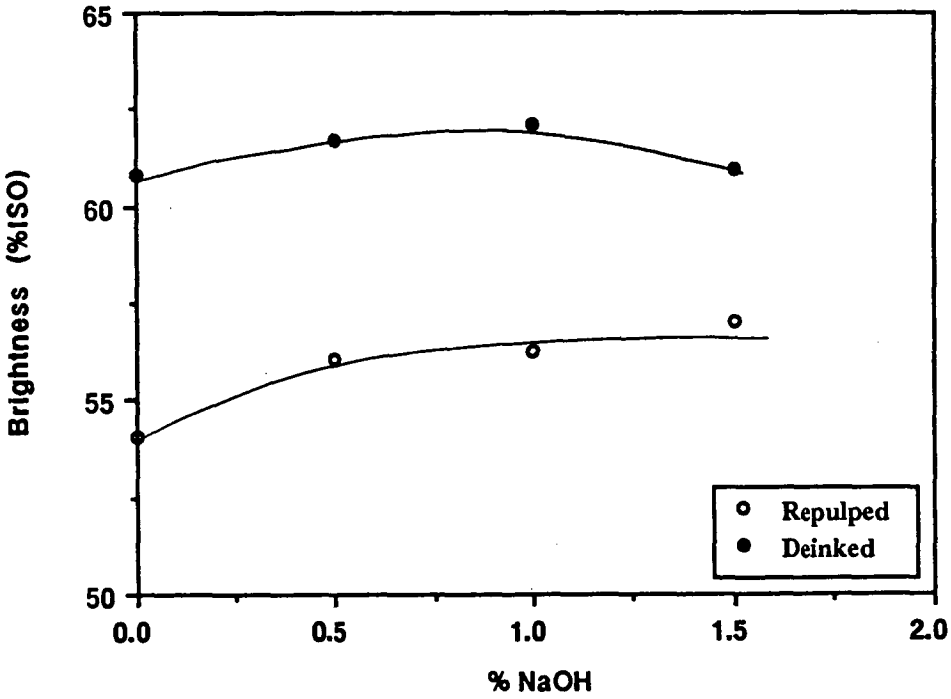

Figure 3.5. Effect of NaOH addition (as % o.d. fibre) on brightness of pulp after pulping and flotation for deinking of 70/30 mixture of ONP/OMG using surfactant C. Pulping conditions: 1% H_2O_2, 1% sodium silicate, 0.2% DTPA, 0.4% surfactant C; time 20 mins; temperature 50°C; consistency 8%. Flotation conditions: time 6 mins; temperature 50°C; consistency 1%.

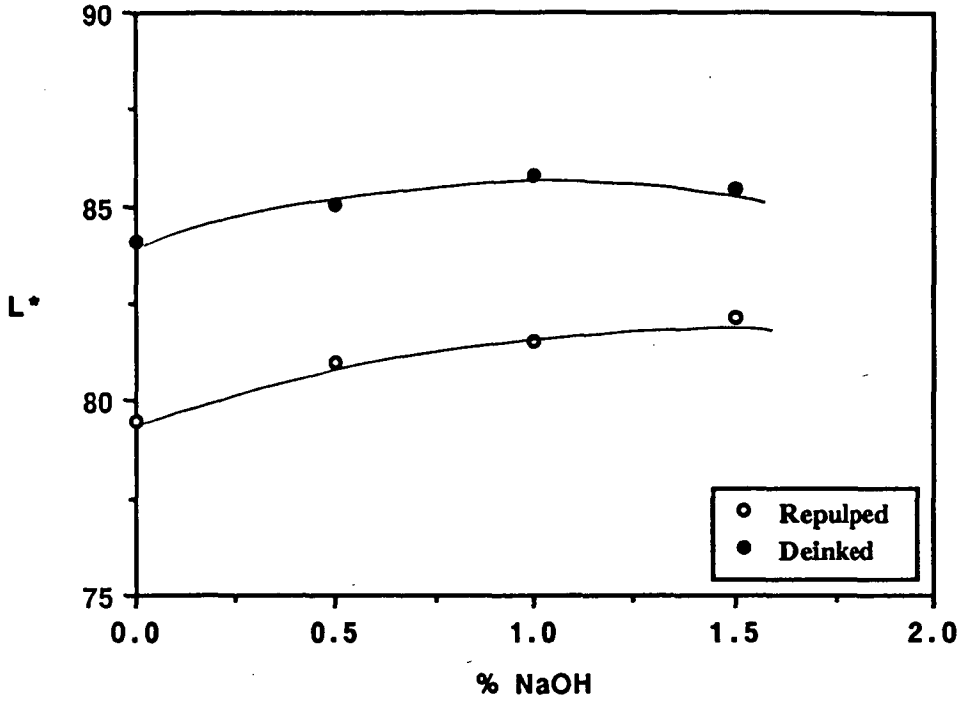

Figure 3.6. Effect of NaOH addition (as % o.d. fibre) on L* of pulp after pulping and flotation for deinking of 70/30 mixture of ONP/OMG using surfactant C. Pulping and flotation conditions as in Figure 3.5.

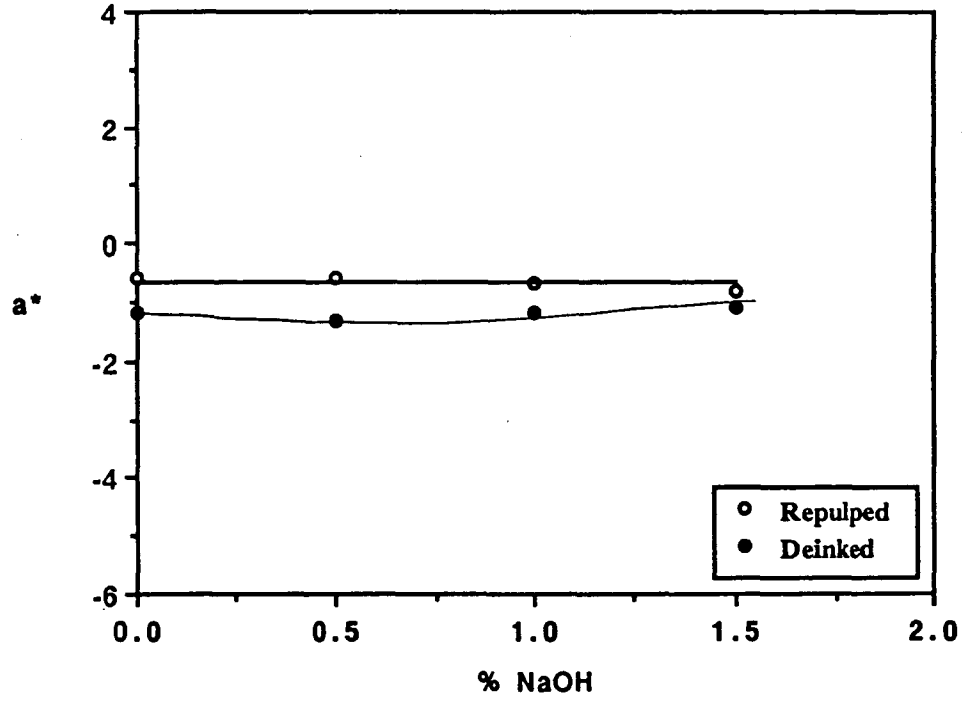

Figure 3.7. Effect of NaOH addition (as % o.d. fibre) on a* of pulp after pulping and flotation for deinking of 70/30 mixture of ONP/OMG using surfactant C. Pulping and flotation conditions as in Figure 3.5.

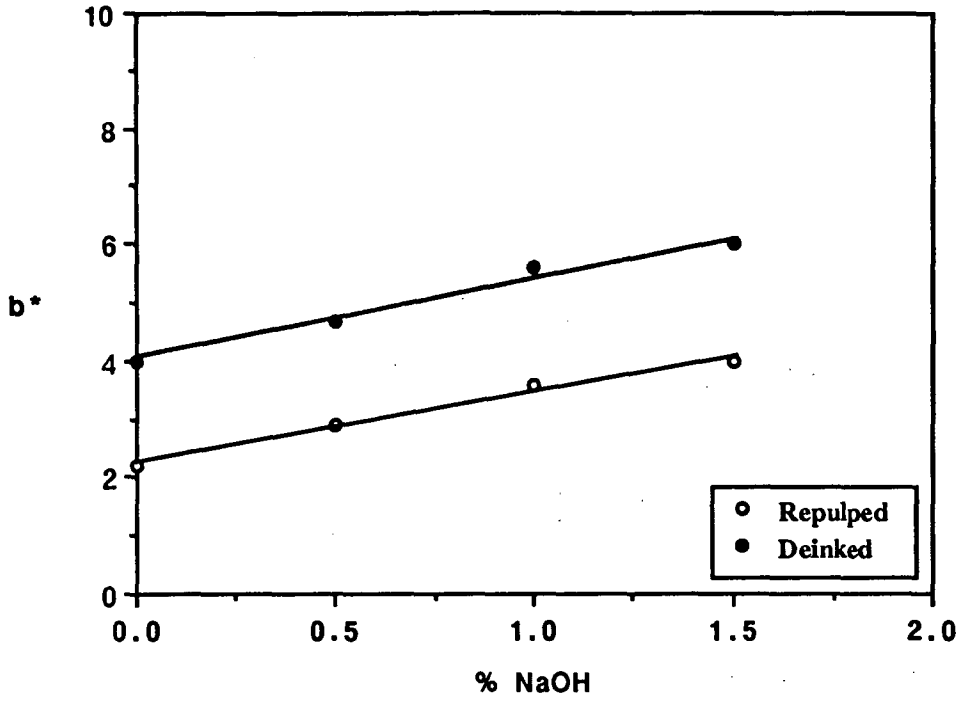

Figure 3.8. Effect of NaOH addition (as % o.d. fibre) on b* of pulp after pulping and flotation for deinking of 70/30 mixture of ONP/OMG using surfactant C. Pulping and flotation conditions as in Figure 3.5.

Repeating the experiment by using a different surfactant (surfactant C) generally shows similar trends as those observed before (surfactant A), although they differ in the extent they increase or decrease with variation in the initial amount of NaOH.

The increase in the brightness of pulp after pulping with increasing initial amount of NaOH is still observable (Figure 3.5), suggesting that alkali conditions are necessary in the pulping stage for both surfactant A and C.

It seems also there is a maximum in the brightness response after flotation with increasing initial amount of NaOH applied, where application of NaOH higher than 1% favours the yellowing reaction in the flotation stage.

It is generally known that in peroxide bleaching there is competition between two reactions as alkalinity changes. They are: (i) chromophore removal or peroxide bleaching, and (ii) alkaline darkening or chromophore formation. The presence of a maximum in brightness after flotation reflects this competition. Above 1% application

of NaOH, alkali darkening predominates over chromophore removal. The value of b* (Figure 3.8) appears to be more affected by the alkali darkening reaction that is favoured by high pH.

3.2.2. Effects of flotation pH

In an attempt to get more insight into the effects of alkalinity in flotation deinking, it was decided to do some experiments where the pH in the flotation stage was adjusted and the initial amount of NaOH applied in the pulping stage was fixed. The application of 1%NaOH in the pulping stage was chosen to ensure that there was enough alkalinity for the pulping and ink detachment from the fibre to be successful.

The experiments were done on deinking of 70/30 mixture of offset printed newspaper and coated magazines by using the deinking surfactants A and C. In the flotation stage, pH of the pulp slurry was adjusted to a desired value by the addition of NaOH or HCl.

The plots in Figures 3.9 to 3.16 show the changes in brightness and colour, L* a* b* values, for the pulp after flotation as well as after the pulping stage. Since there are no process variable changes made in the pulping stage, it is expected that the response will remain constant (represented by the empty dots). They are plotted in the graph for reference for the changes observed in the response after flotation stage due to pH changes, which are represented by filled dots.

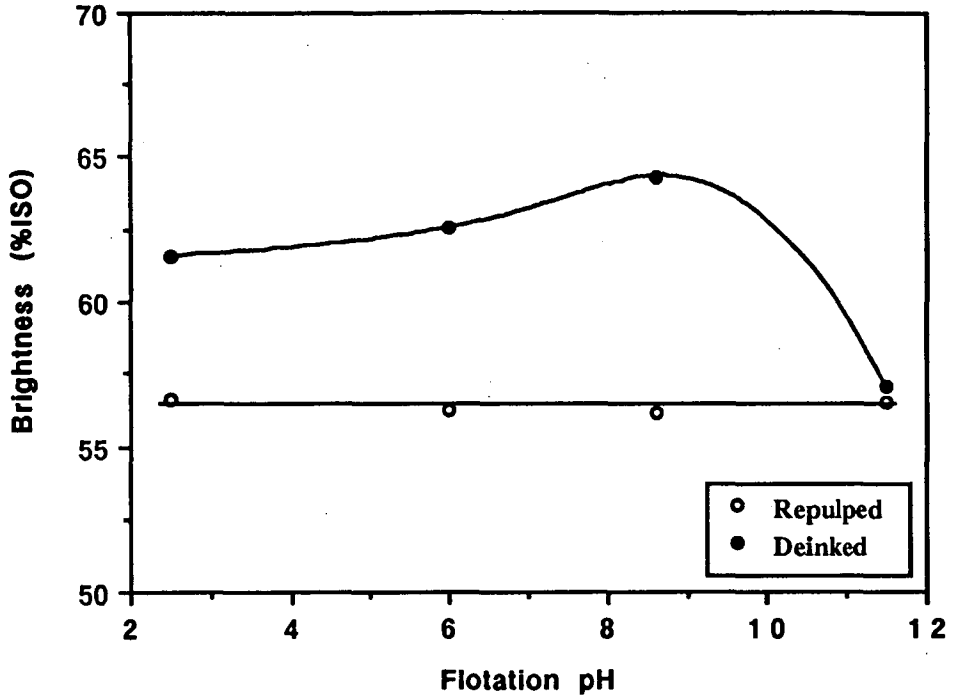

Figure 3.9. Effect of pH adjustment prior to flotation stage on brightness of pulp for deinking of 70/30 mixture of ONP/OMG using surfactant A. Pulping conditions: 1%NaOH, 1% H_2O_2, 1% sodium silicate, 0.2% DTPA, 0.4% surfactant A; time 20 mins; temperature 50°C; consistency 8%. Flotation conditions: time 6 mins; temperature 50°C; consistency 1%.

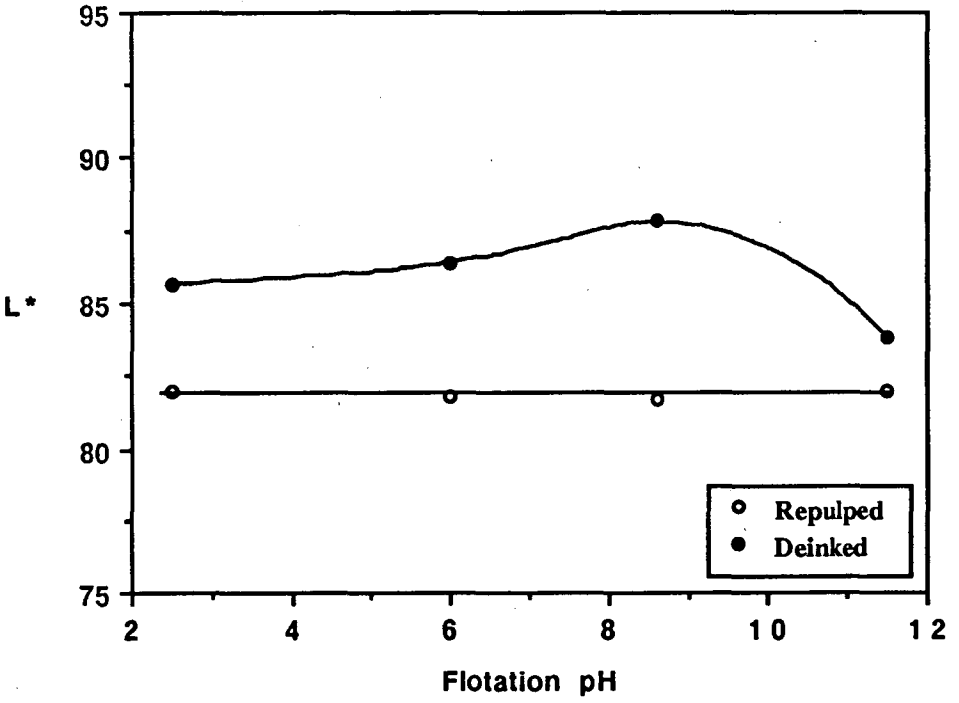

Figure 3.10. Effect of pH adjustment prior to flotation stage on L* of pulp for deinking of 70/30 mixture of ONP/OMG using surfactant A. Pulping and flotation conditions as in Figure 3.9.

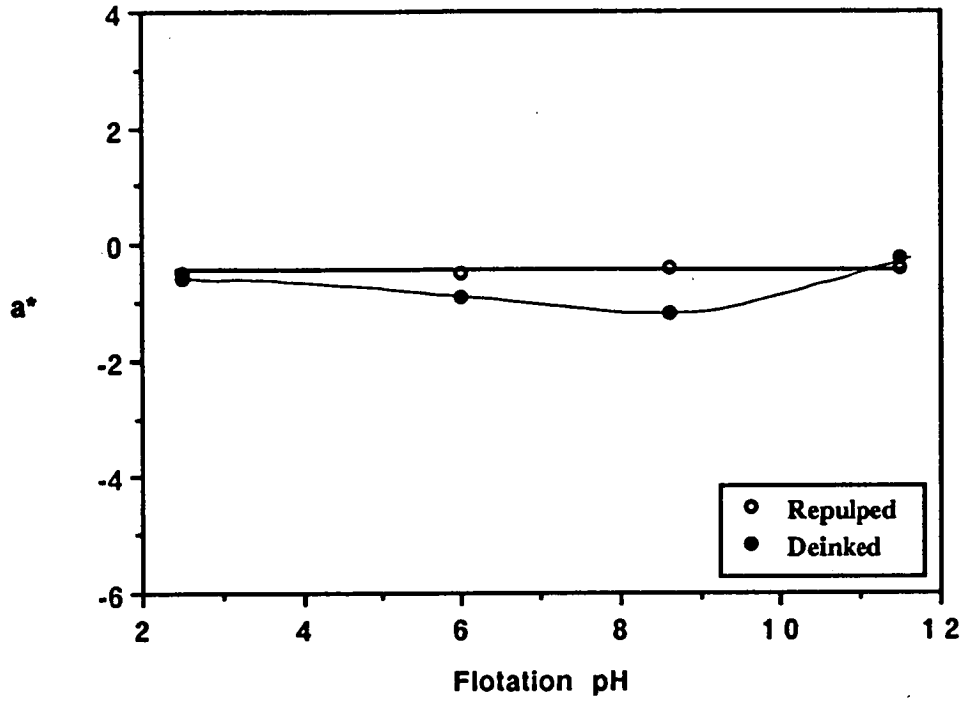

Figure 3.11. Effect of pH adjustment prior to flotation stage on a* of pulp for deinking of 70/30 mixture of ONP/OMG using surfactant A. Pulping and flotation conditions as in Figure 3.9.

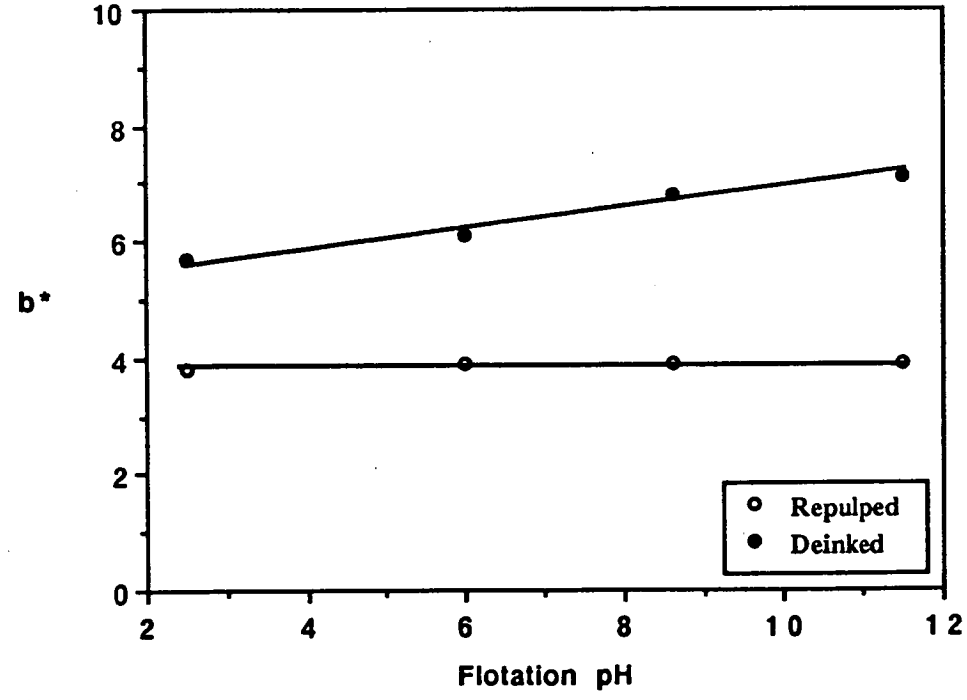

Figure 3.12. Effect of pH adjustment prior to flotation stage on b* of pulp for deinking of 70/30 mixture of ONP/OMG using surfactant A. Pulping and flotation conditions as in Figure 3.9.

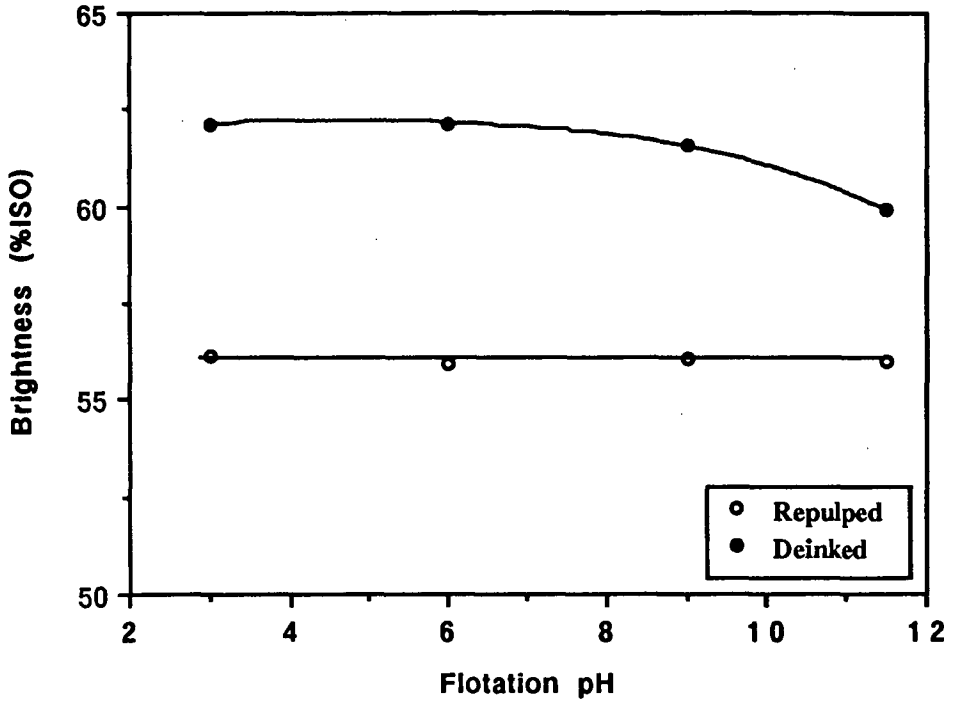

Figure 3.13. Effect of pH adjustment prior to flotation stage on brightness of pulp for deinking of 70/30 mixture of ONP/OMG using surfactant C. Pulping conditions: 1%NaOH, 1% H_2O_2, 1% sodium silicate, 0.2% DTPA, 0.4% surfactant C; time 20 mins; temperature 50°C; consistency 8%. Flotation conditions: time 6 mins; temperature 50°C; consistency 1%.

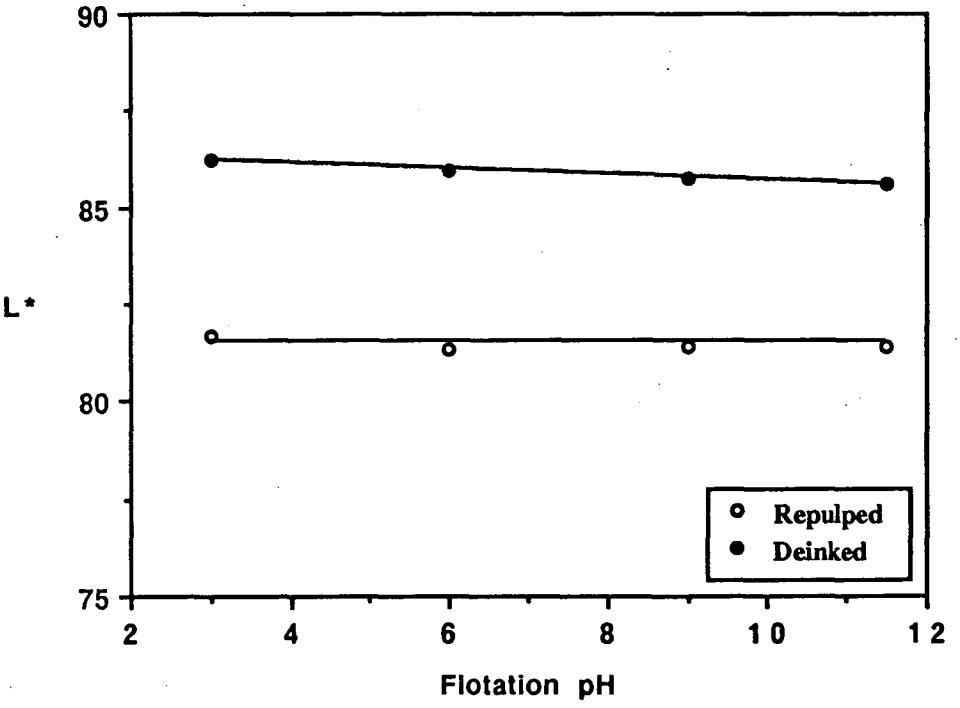

Figure 3.14. Effect of pH adjustment prior to flotation stage on L* of pulp for deinking of 70/30 mixture of ONP/OMG using surfactant C. Pulping and flotation conditions as in Figure 3.13.

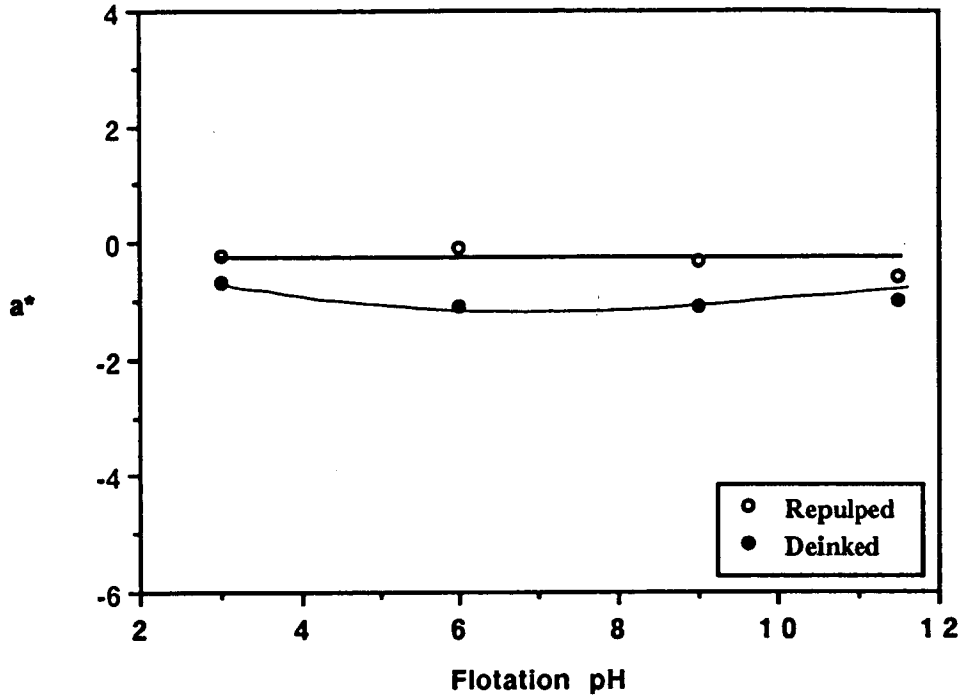

Figure 3.15. Effect of pH adjustment prior to flotation stage on a* of pulp for deinking of 70/30 mixture of ONP/OMG using surfactant C. Pulping and flotation conditions as in Figure 3.13.

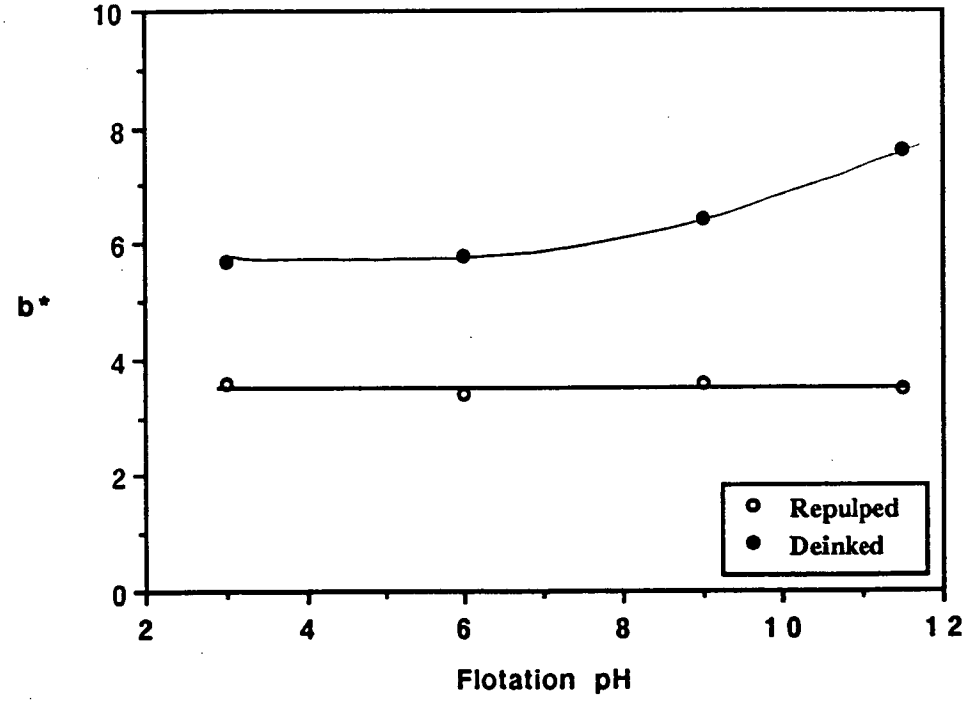

Figure 3.16. Effect of pH adjustment prior to flotation stage on b* of pulp for deinking of 70/30 mixture of ONP/OMG using surfactant C. Pulping and flotation conditions as in Figure 3.13.

The results once again illustrate that b* value is increasing with increasing pH (as shown in Figures 3.12 and 3.16), which gives further evidence that the b* value or the yellowness of the pulp is significantly affected by pH. Higher pH in the flotation stage favours the chromophore formation, which is reflected in the higher b* values.

The results, in Figures 3.9 and 3.13, indicate that the two surfactants behave differently as pH is varied. The brightness responses illustrate that there is an optimum pH at which the brightness response is at a maximum. The presence of an optimum pH is more noticeable for surfactant A (Figure 3.9). Up to pH ~8.5, the brightness increases as the flotation pH is increased. Above pH ~8.5, further increase in flotation pH results in a decline in the brightness response. For surfactant C (Figure 3.13), the brightness response is fairly constant up to pH ~8.5, above which the brightness response starts to decline slightly. The loss of brightness at higher pH can be partly accounted for by the increasing yellowing reaction or chromophore formation, as illustrated by higher b* values. However, it is unlikely that yellowing reaction or chromophore formation is solely responsible for brightness loss, considering the different response for different surfactant type. It is possible for pH to affect the performance of surfactants in ink removal process. However, the mechanism of how pH could affect the performance of surfactants could not be explained due to lack of information on the exact composition of the surfactants.

The response of L* value for surfactant A, in Figure 3.10, generally follows that of brightness (Figure 3.9), where L* value increases with increasing flotation pH up to ~8.5 and then decreases beyond pH ~8.5. In the case of surfactant C, the response of L* value seems to decrease slightly with increasing flotation pH (Figure 3.14). This might suggest that, since L* values represent the greyness of the pulp and therefore ink removal [5], flotation pH hardly affected the performance of surfactant C in the ink removal process. However, further evidence is required to support this statement.

The a* values for both surfactants (Figures 3.11 and 3 .15) are hardly affected by changes in flotation pH over the pH range studied.

3.3. Effects of temperature

The effects of temperature in both the pulping and flotation stages were also investigated and the results are shown in Figures 3.17 to 3.20 for surfactant A and Figures 3.21 to 3.24 for surfactant C. Figures 3.17a and 3.21a show the effect on brightness upon varying the temperature in the pulping stage (maintaining the flotation temperature at 50°C), and Figures 3.17b and 3.21b show the effect on brightness upon varying the temperature in the flotation stage (maintaining the pulping temperature at 50°C). The results clearly show that there is an enhancement of brightness response associated with increased flotation temperature in the range 20° to 50°C. The benefit on increasing the temperature through this range corresponds to an improvement of ~3 brightness units (Figures 3.17b and 3.21b). In contrast, increasing the temperature in the pulping stage (maintaining the flotation temperature at 50°C) has little significant impact (Figure 3.17a) or no effect (Figure 3.21a) on the brightness achieved.

The L* value, as shown in Figure 3.18 and 3.22, gave rise to similar trends as did the brightness measurements at 457 nm. However, for surfactant C, temperature increase in the pulping stage (maintaining the flotation temperature at 50°C) has slightly more impact on the L* value (Figure 3.22a) than on the brightness (Figure 3.21a). The yellowness of the pulp as represented by b* value generally increased as temperature increased (Figures 3.20 and 3.24). There was very little change in the a* value (Figures 3.19 and 3.23) with temperature change.

The different responses of the surfactants A and C toward temperature changes suggest that the performance of surfactant is affected by temperature. The nature and chemical composition of the surfactants is responsible for this different behaviour. It was suggested by some researchers that for surfactant to be effective in

flotation the surfactant molecules should form aggregates [6]. Increasing temperature favours the surfactant molecules coming more closely together and forming aggregates.

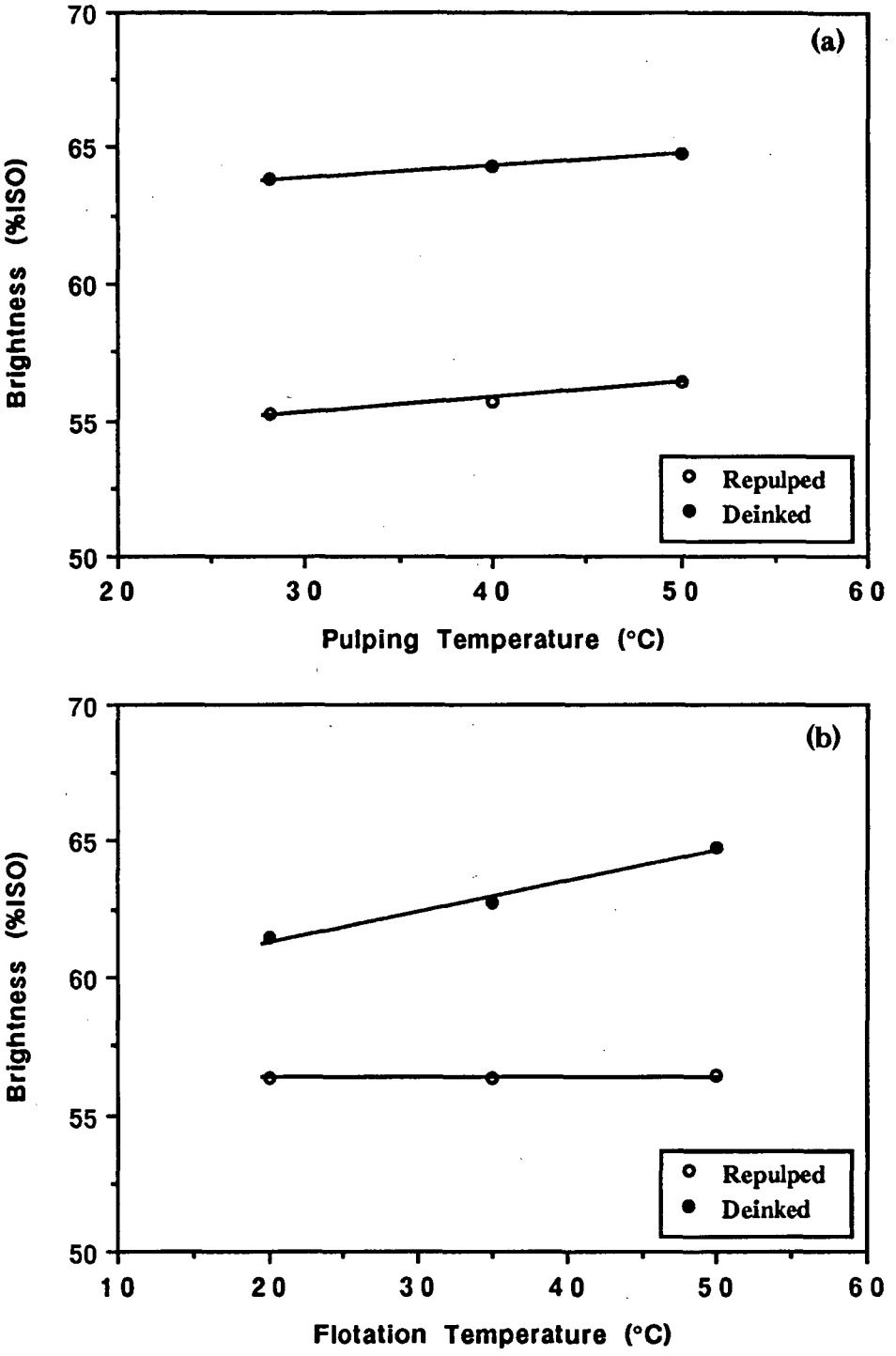

Figure 3.17. Effect of temperature during (a) pulping with constant flotation temperature of 50°C, and (b) flotation with constant pulping temperature of 50°C on brightness for deinking of 70/30 mixture of ONP/OMG using surfactant A. Pulping conditions: 1%NaOH, 1% H_2O_2, 1% sodium silicate, 0.2% DTPA, 0.4% surfactant A; time 20 mins; consistency 8%. Flotation conditions: time 6 mins; consistency 1%, pH 8.5.

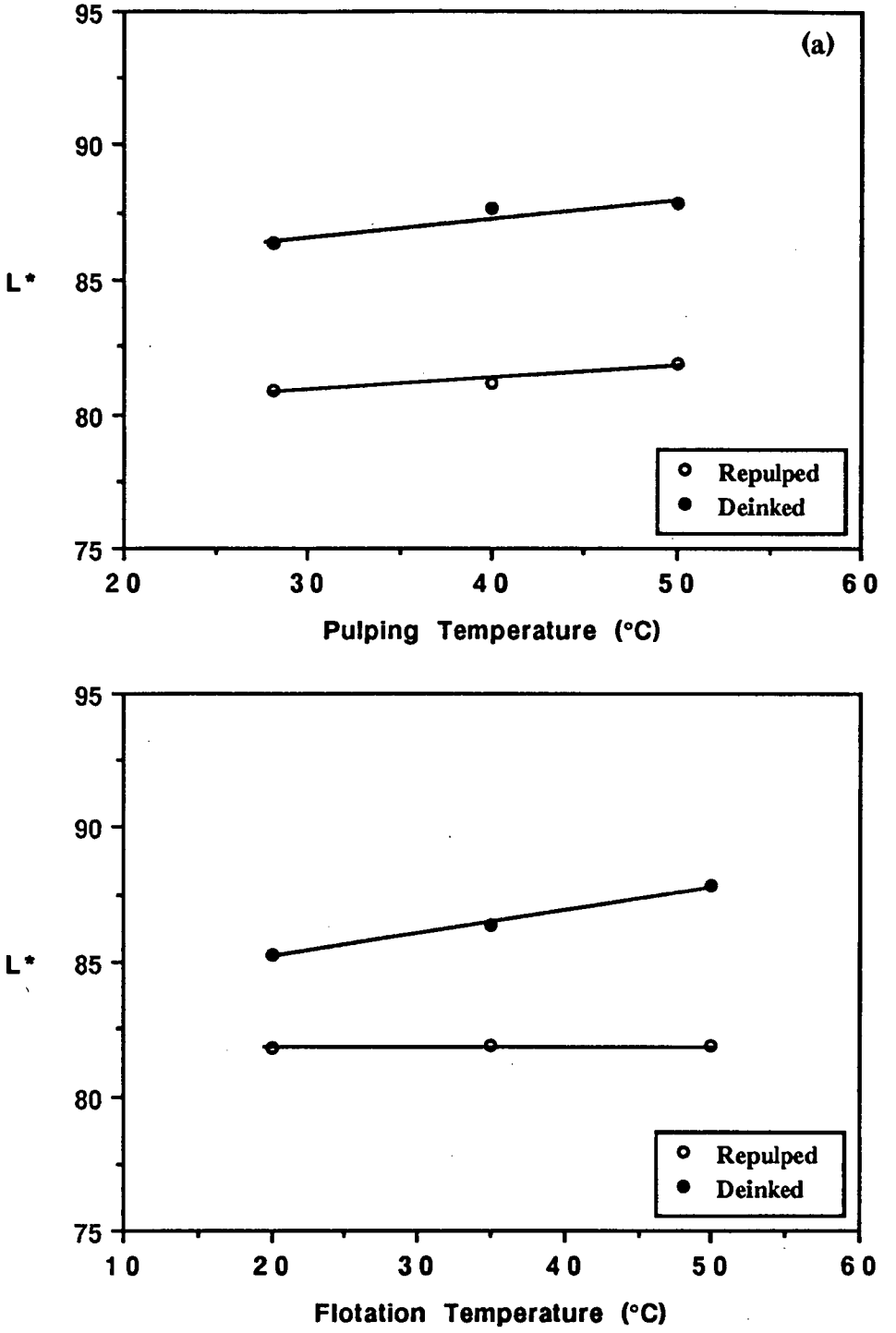

Figure 3.18. Effect of temperature during (a) pulping with constant flotation temperature of 50°C, and (b) flotation with constant pulping temperature of 50°C on L* for deinking of 70/30 mixture of ONP/OMG using surfactant A. Pulping and flotation conditions as in Figure 3.17.

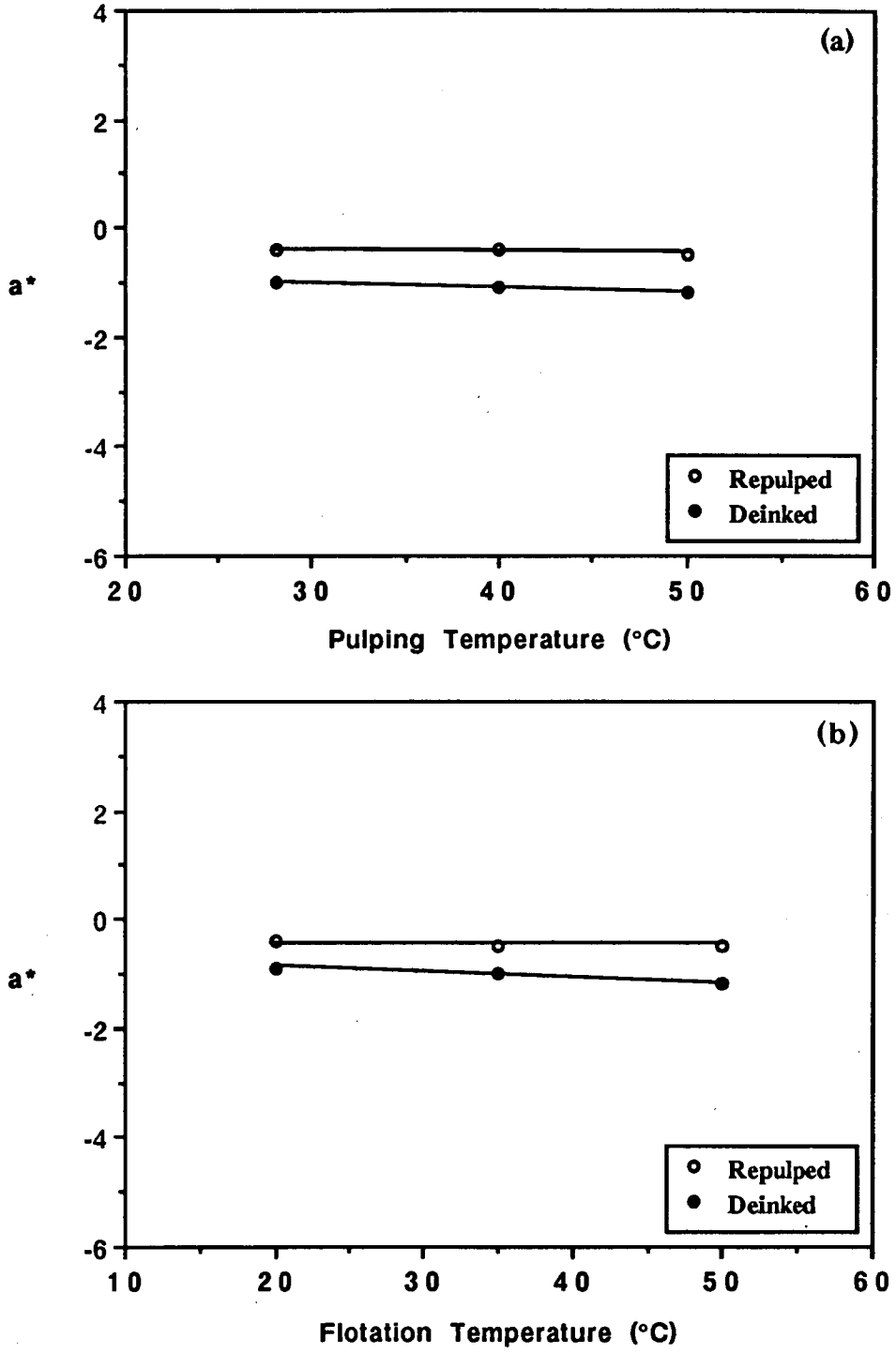

Figure 3.19. Effect of temperature during (a) pulping with constant flotation temperature of 50°C, and (b) flotation with constant pulping temperature of 50°C on a* for deinking of 70/30 mixture of ONP/OMG using surfactant A. Pulping and flotation conditions as in Figure 3.17.

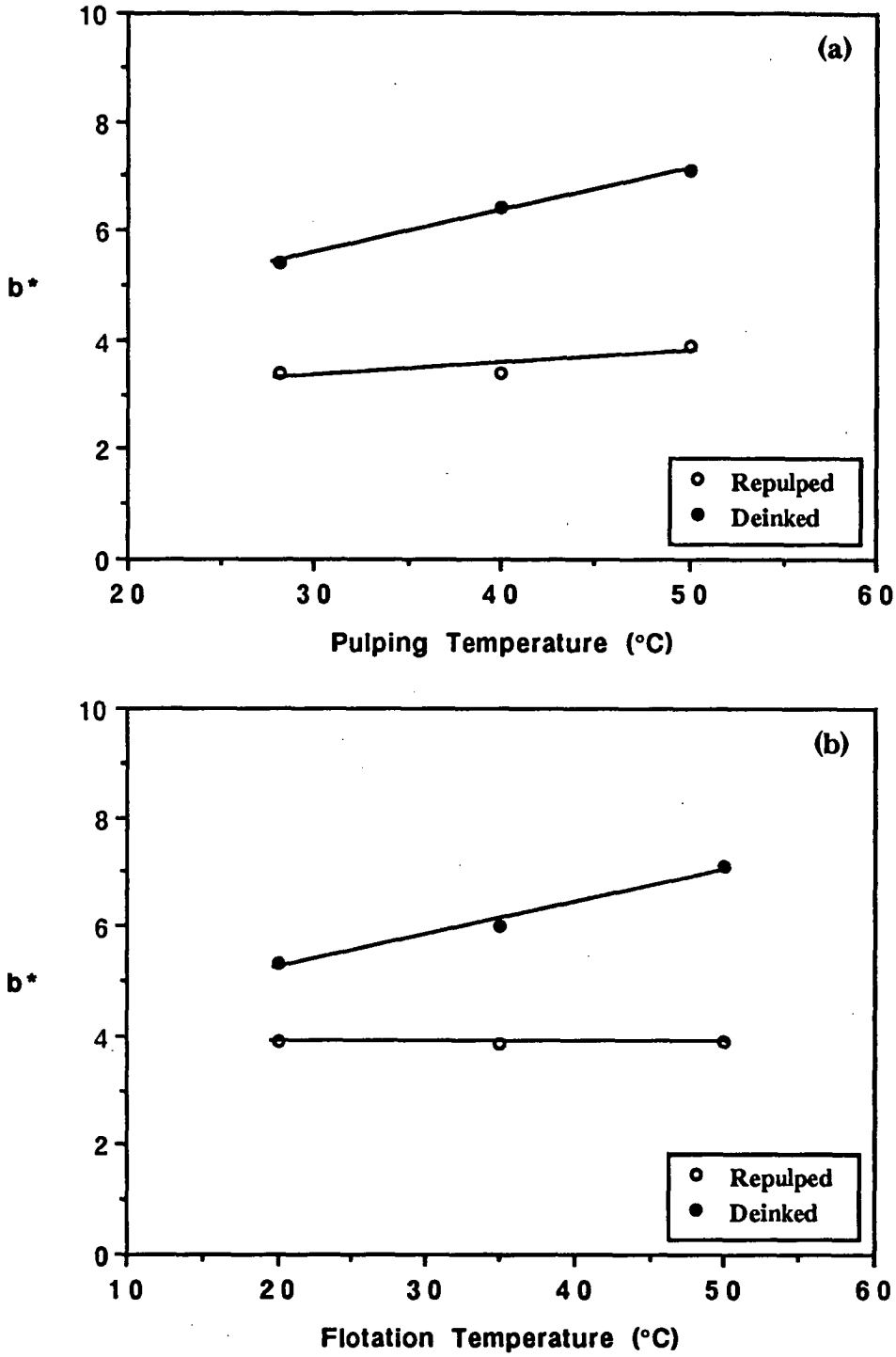

Figure 3.20. Effect of temperature during (a) pulping with constant flotation temperature of 50°C, and (b) flotation with constant pulping temperature of 50°C on b* for deinking of 70/30 mixture of ONP/OMG using surfactant A. Pulping and flotation conditions as in Figure 3.17.

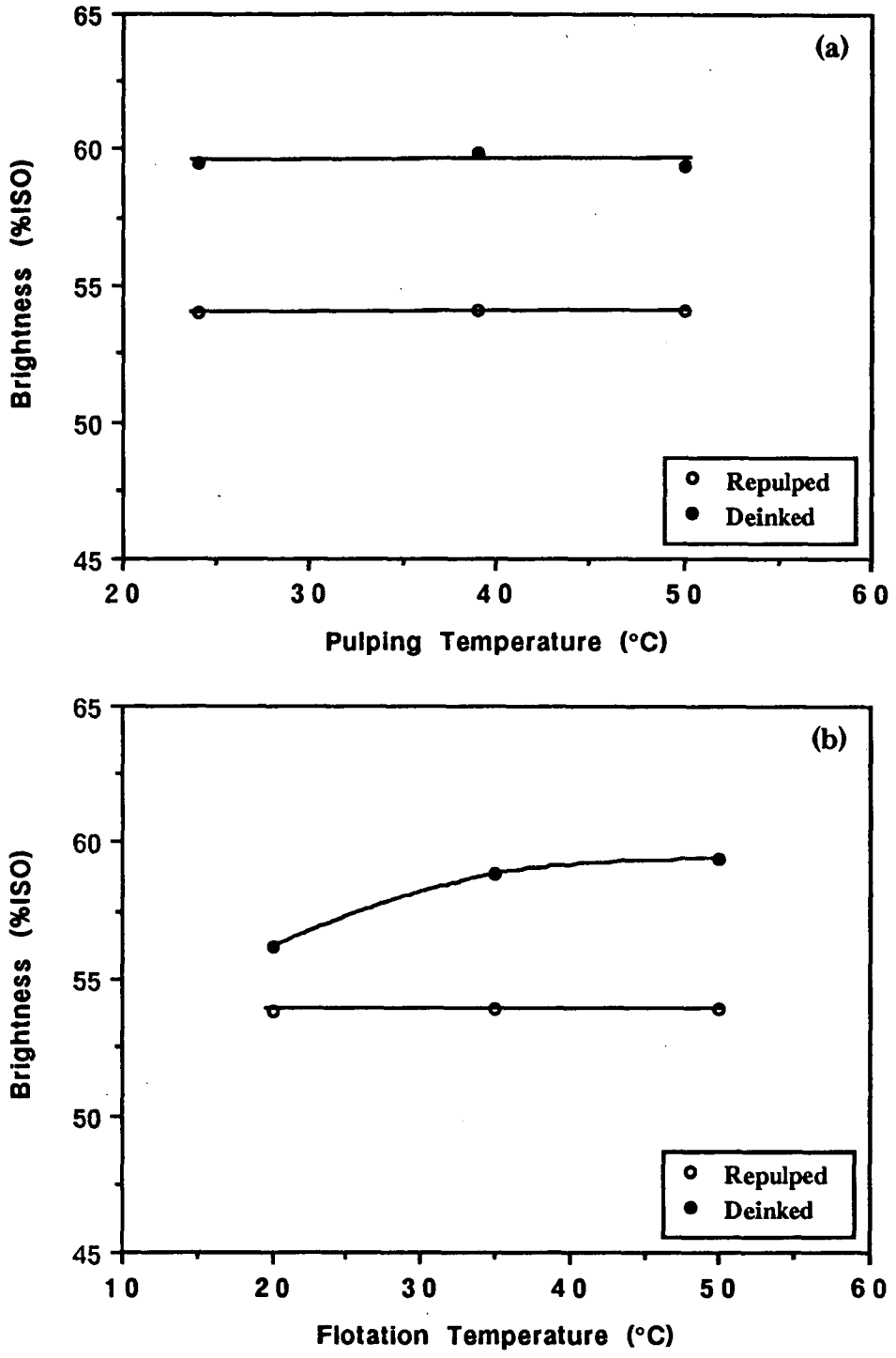

Figure 3.21. Effect of temperature during (a) pulping with constant flotation temperature of 50°C, and (b) flotation with constant pulping temperature of 50°C on brightness for deinking of 70/30 mixture of ONP/OMG using surfactant C. Pulping conditions: 1%NaOH, 1% H_2O_2, 1% sodium silicate, 0.2% DTPA, 0.4% surfactant C; time 20 mins; consistency 8%. Flotation conditions: time 6 mins; consistency 1%, pH 8.5.

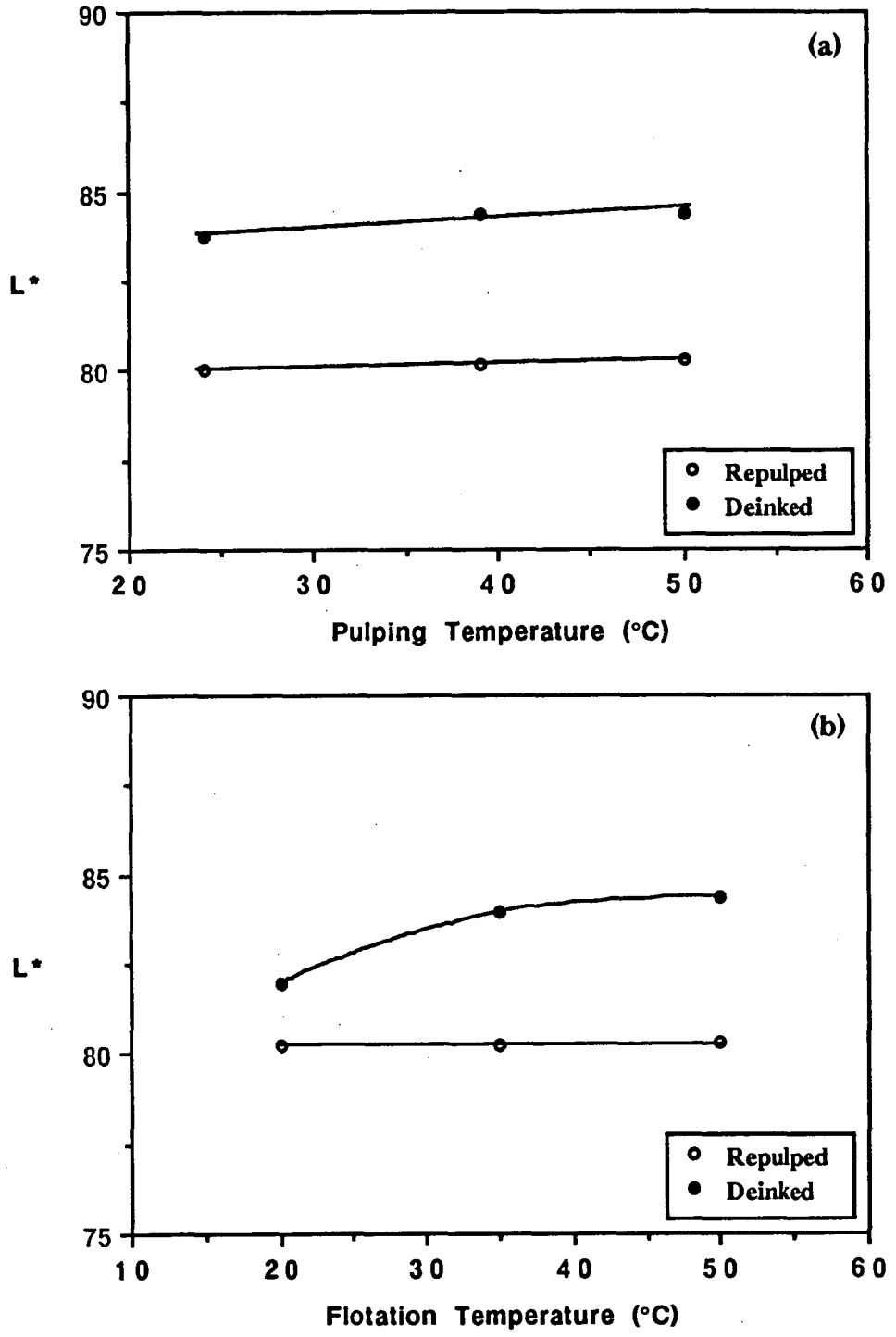

Figure 3.22. Effect of temperature during (a) pulping with constant flotation temperature of 50°C, and (b) flotation with constant pulping temperature of 50°C on L* for deinking of 70/30 mixture of ONP/OMG using surfactant C. Pulping and flotation conditions as in Figure 3.21.

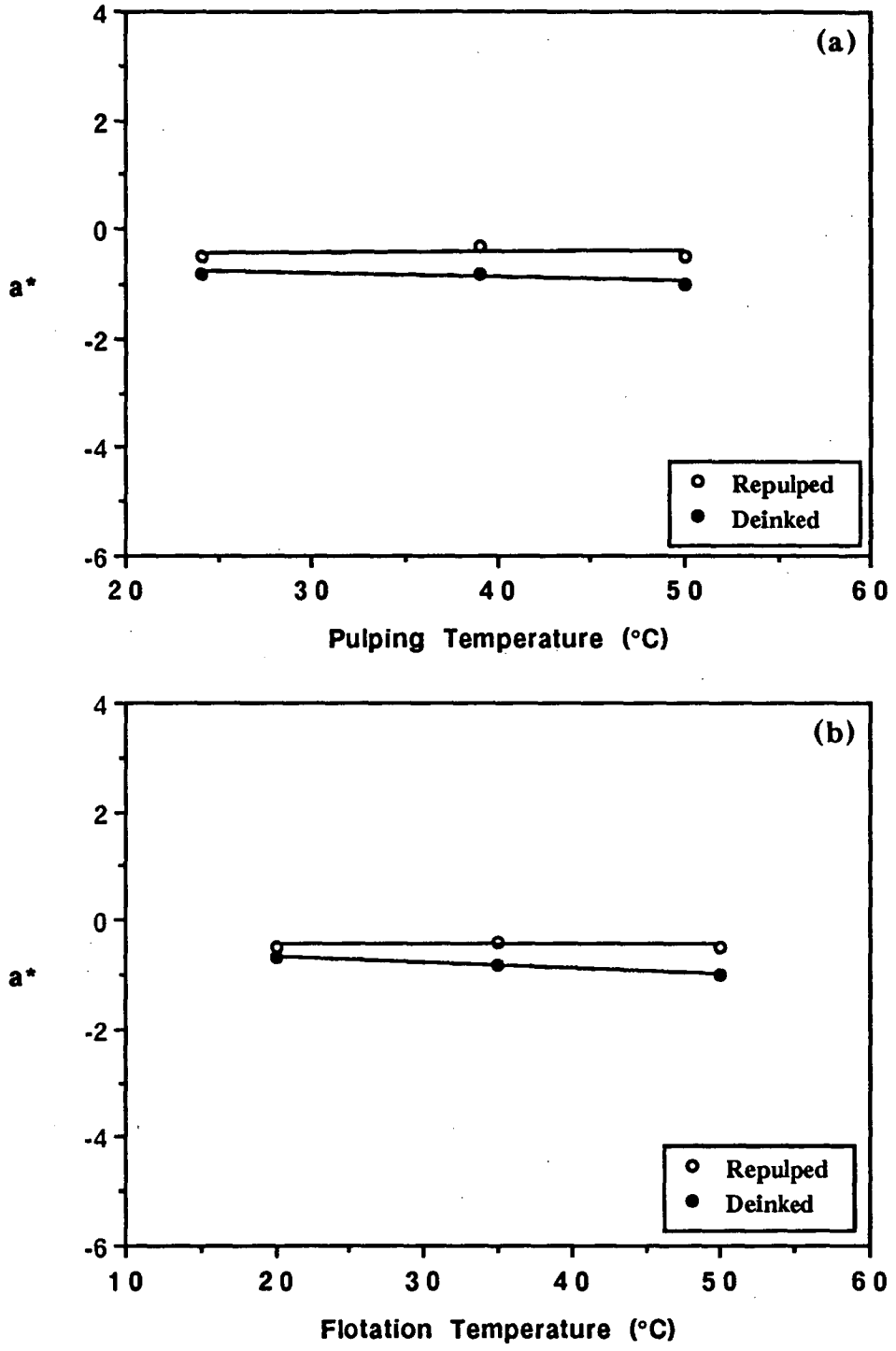

Figure 3.23. Effect of temperature during (a) pulping with constant flotation temperature of 50°C, and (b) flotation with constant pulping temperature of 50°C on a* for deinking of 70/30 mixture of ONP/OMG using surfactant C. Pulping and flotation conditions as in Figure 3.21.

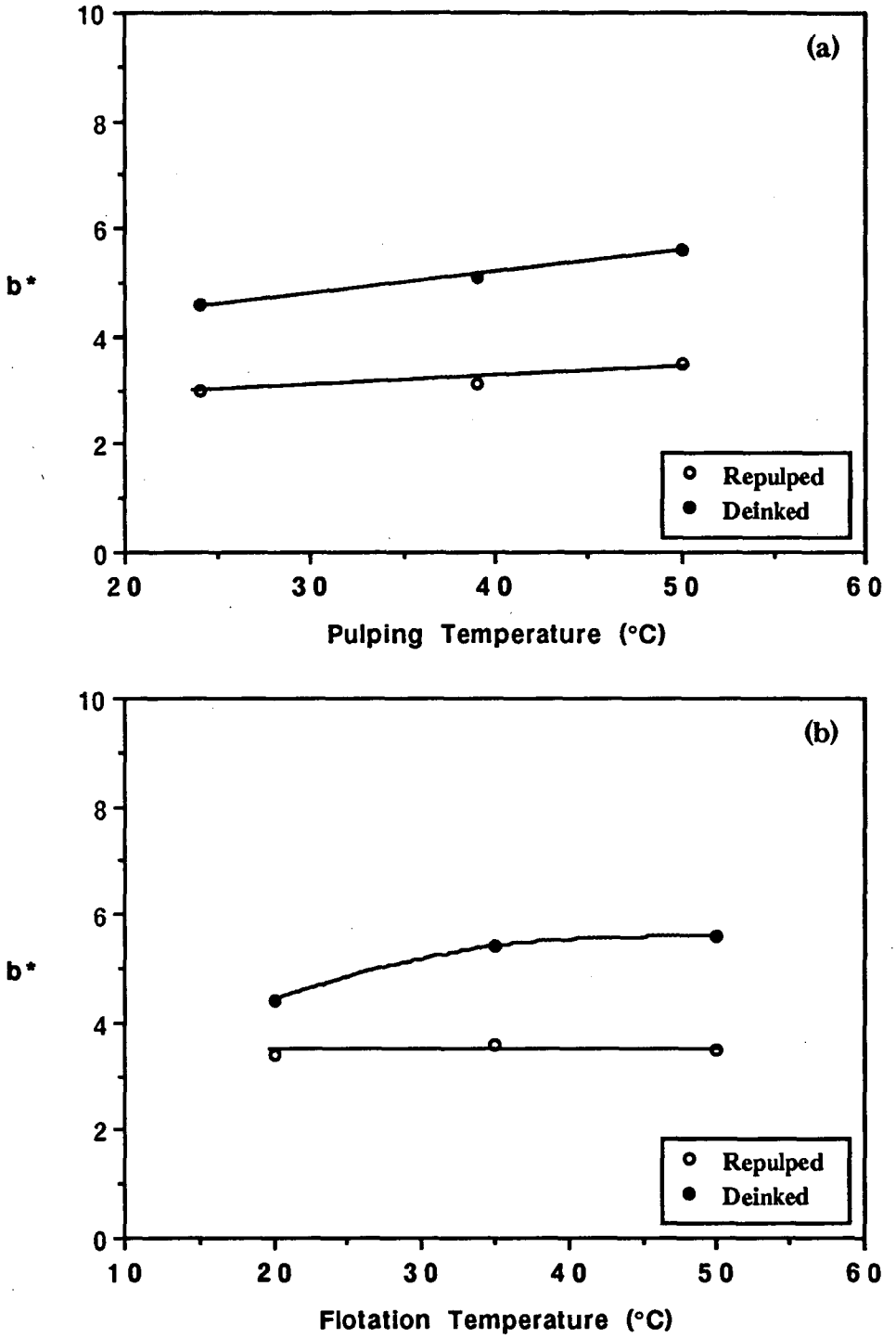

Figure 3.24. Effect of temperature during (a) pulping with constant flotation temperature of 50°C, and (b) flotation with constant pulping temperature of 50°C on b* for deinking of 70/30 mixture of ONP/OMG using surfactant C. Pulping and flotation conditions as in Figure 3.21.

3.4. Summary

An alkali environment in the pulping stage is crucial to ensure successful ink detachment from fibres. However, high alkalinity for wood-containing furnishes, such as 70/30 mixture of offset printed newspaper and coated magazines, can induce a phenomenon known as alkaline darkening which is due to the formation of chromophores. To counter the formation of chromophores, hydrogen peroxide is added in the pulping stage, which is responsible for chromophores removal.

In the flotation stage, pH adjustment in some cases is beneficial in order to minimise the yellowing of the pulp due to high alkalinity. However, it also has been illustrated that the performance of the surfactant in ink removal in flotation stage is also influenced by pH.

Temperature is also an important factor which accounts for variation in deinking efficiency as measured by brightness. In the range 20° to 50°C, increasing temperature in the flotation stage (maintaining the pulping temperature at 50°C) is more beneficial than increasing temperature in the pulping stage (maintaining the flotation temperature at 50°C).

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Chapter 4

Feedstock Composition in Flotation Deinking

4.1. Introduction

One of the variables in flotation deinking beside the pulping and flotation conditions is the deinking feedstock itself. Newspaper and magazines have been traditionally used as the feedstock for flotation deinking. Variables within the feedstock paper, such as type of ink, method of printing, paper grade, as well as the proportion of newspaper and magazines in the feedstock, can all affect the efficiency of deinking.

The old newspaper (ONP) sample used in this study was offset printed newspaper. It was about 2-3 months old. The old magazines (OMG) sample was represented by a selection of magazines (eg. Cleo, Women's Weekly etc.). The age of these magazines was approximately 6-12 months. The OMG sample has an ash content of 26%.

The first part of the study on the variation in feedstock composition in flotation deinking aims to investigate the deinking of newspaper and magazines individually and study the deinking efficiency in terms of brightness and colour (in L*, a*, b* scales). The second part aims to look at the effect of magazines (OMG) inclusion in the flotation deinking of newspaper (ONP).

Surfactant sample B was chosen to investigate the variation in feedstock composition. Surfactant sample B is a multi-component surfactant, its main components are combinations of C_{18} fatty acid soaps, similar to surfactant sample A used to study the effect of pH and temperature in Chapter 3.

4.2. Deinking of offset printed newspaper and magazines

In this experiment, newspaper (ONP) and magazines (OMG) were deinked separately. The effects of surfactant addition on deinking efficiency in terms of brightness, L* and b* were examined.

4.2.1. Deinking of offset printed newspaper

The effect of surfactant addition on deinking of 100% ONP on brightness is shown in Figure 4.1. Only a small (2 unit) increase in brightness occurs on flotation. This is not uncommon. This is due to low ink content in newspapers. Also the ISO brightness of the non-inked areas of ONP is around 60%.

Figure 4.1 shows that above the addition level of 0.6% surfactant B the brightness response starts to decline. This effect is more noticeable in the brightness response after pulping.

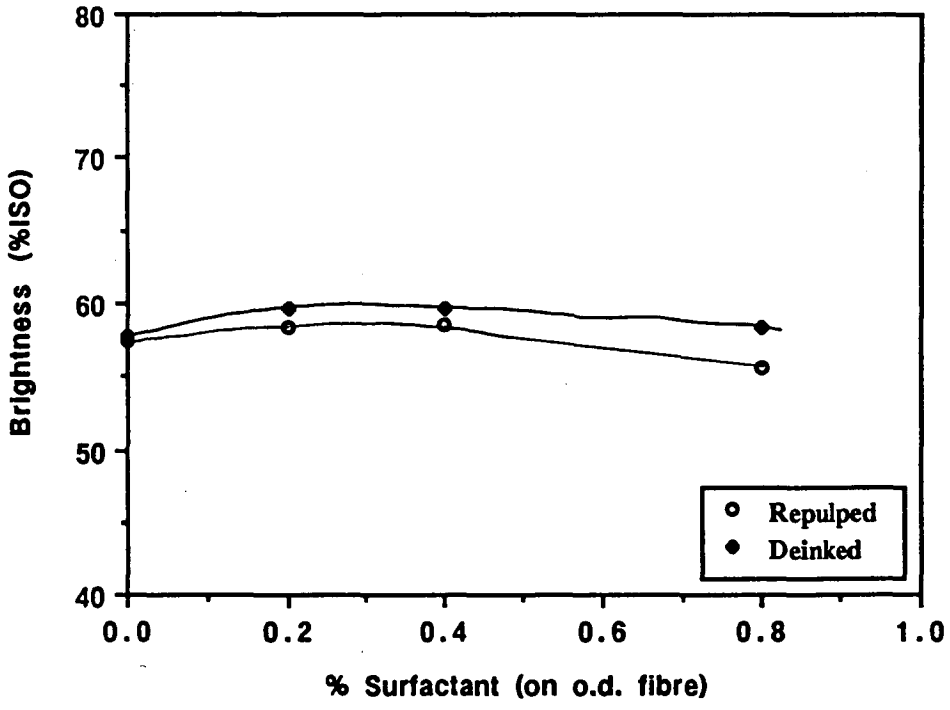

Figure 4.1. Effect of Surfactant B addition (as % o.d. fibre) on brightness of pulp after pulping and flotation for deinking of ONP. Pulping conditions: 1% NaOH, 1% H_2O_2, 1% sodium silicate, 0.2% DTPA; time 20 mins; temperature 50°C; consistency 8%. Flotation conditions: time 6 mins; temperature 50°C; consistency 1%.

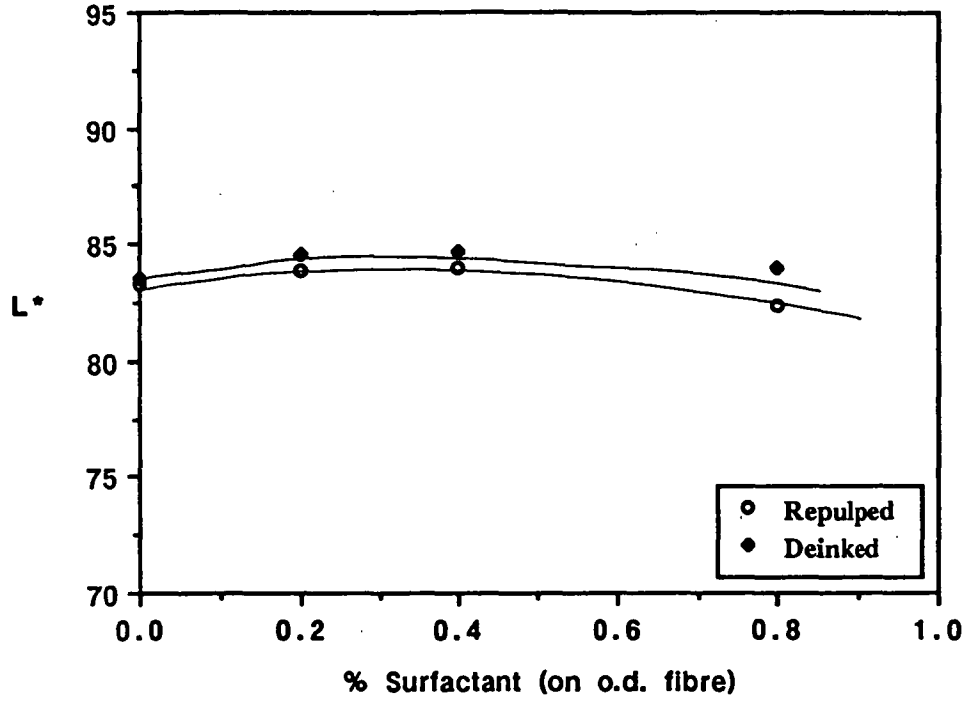

Figure 4.2. Effect of Surfactant B addition (as % o.d. fibre) on L* of pulp after pulping and flotation for deinking of ONP. Pulping and flotation conditions as in Figure 4.1.

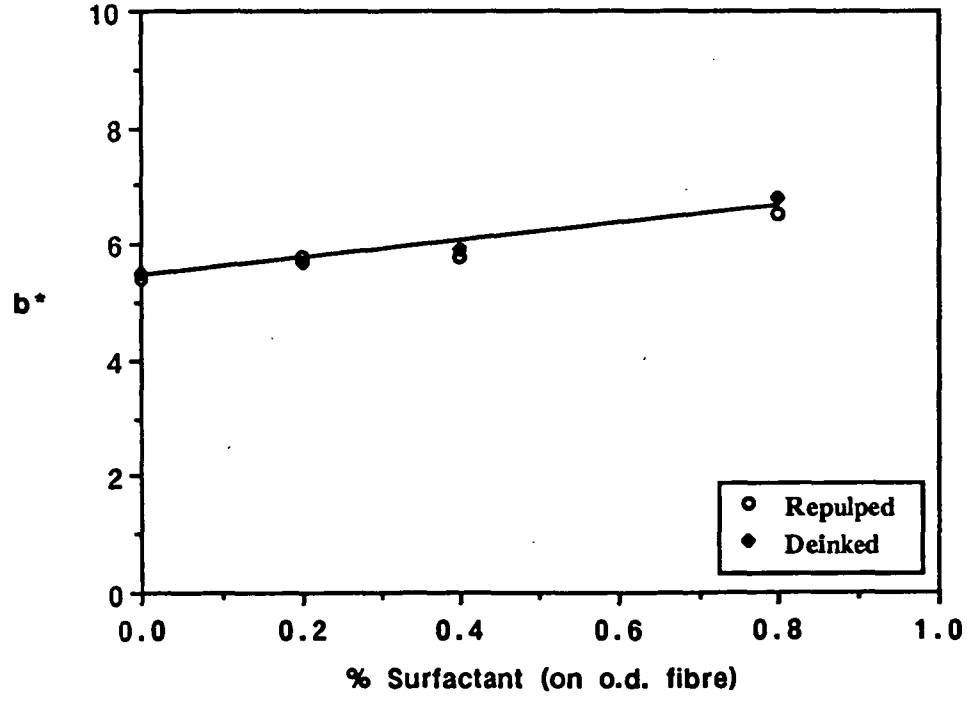

Figure 4.3. Effect of Surfactant B addition (as % o.d. fibre) on b* of pulp after pulping and flotation for deinking of ONP. Pulping and flotation conditions as in Figure 4.1.

The L* response in Figure 4.2 shows a similar trend to the brightness response. It is apparent, from Figures 4.1 and 4.2, that there is an optimum range of surfactant addition level for deinking of 100% ONP, above which the brightness and L* response suffer a loss.

The b* response (Figure 4.3) shows a slight increase as the level of surfactant addition increases. Figure 4.3 also shows that the b* values of the pulp after pulping stage are generally the same as those after flotation stage.

4.2.2. Deinking of magazines

The effect of surfactant addition on brightness on deinking of 100% OMG is shown in Figure 4.4. A 20 unit increase in brightness occurs, which is much higher than that obtained for 100% ONP (Figure 4.1). This is due to a higher ink content in OMG than in ONP. Also, the non-inked areas of OMG have a higher ISO brightness (around 75%) compare to that of ONP.

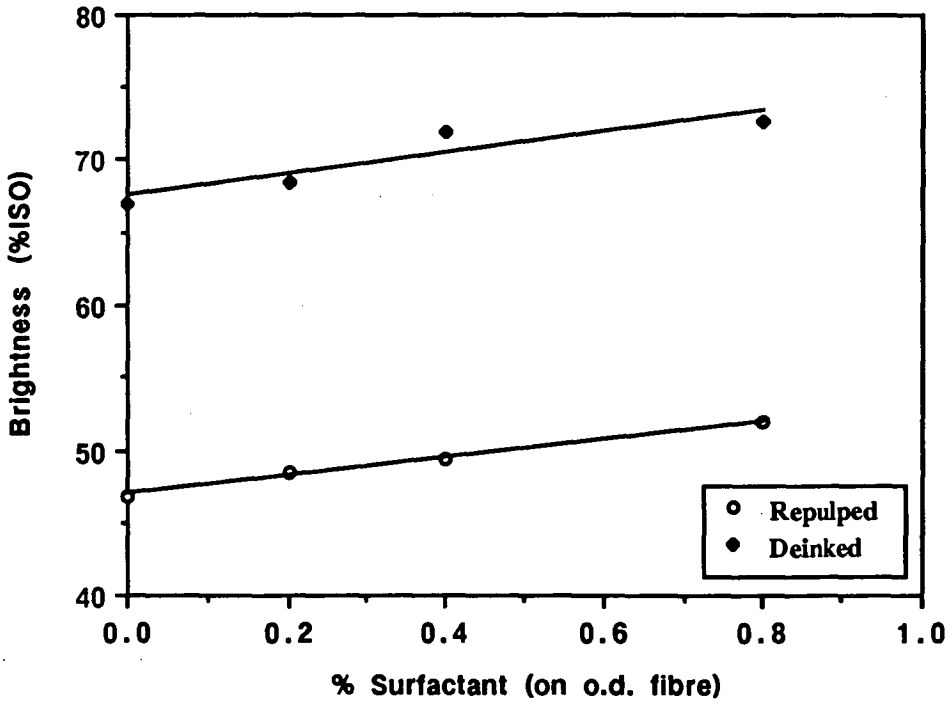

Figure 4.4. Effect of Surfactant B addition (as % o.d. fibre) on brightness of pulp after pulping and flotation for deinking of OMG. Pulping conditions: 1% NaOH, 1% H_2O_2, 1% sodium silicate, 0.2% DTPA; time 20 mins; temperature 50°C; consistency 8%. Flotation conditions: time 6 mins; temperature 50°C; consistency 1%.

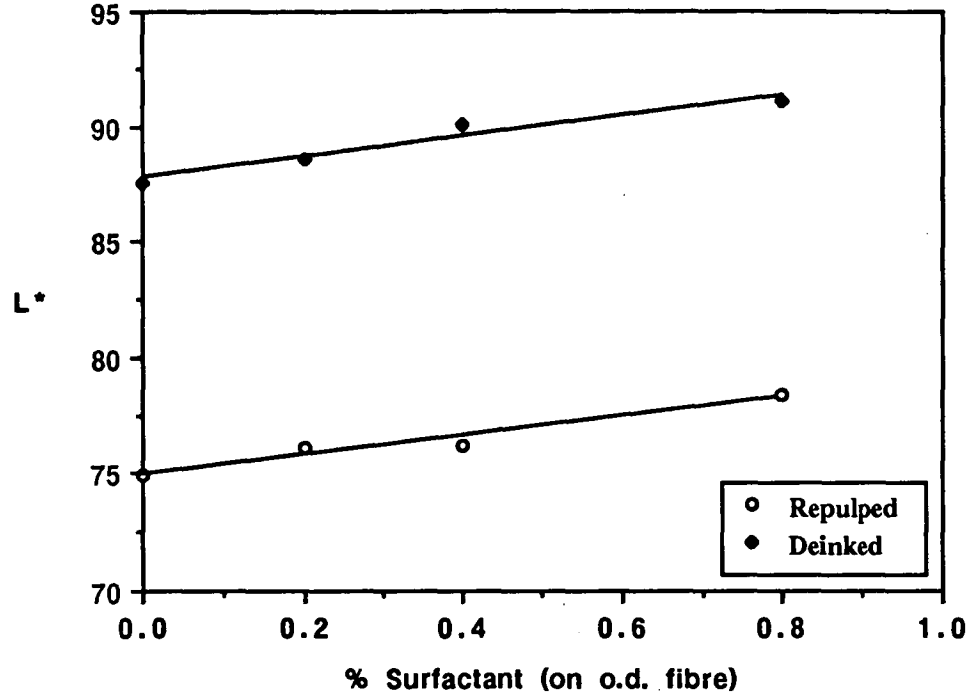

Figure 4.5. Effect of Surfactant B addition (as % o.d. fibre) on L* of pulp after pulping and flotation for deinking of OMG. Pulping and flotation conditions as in Figure 4.4.

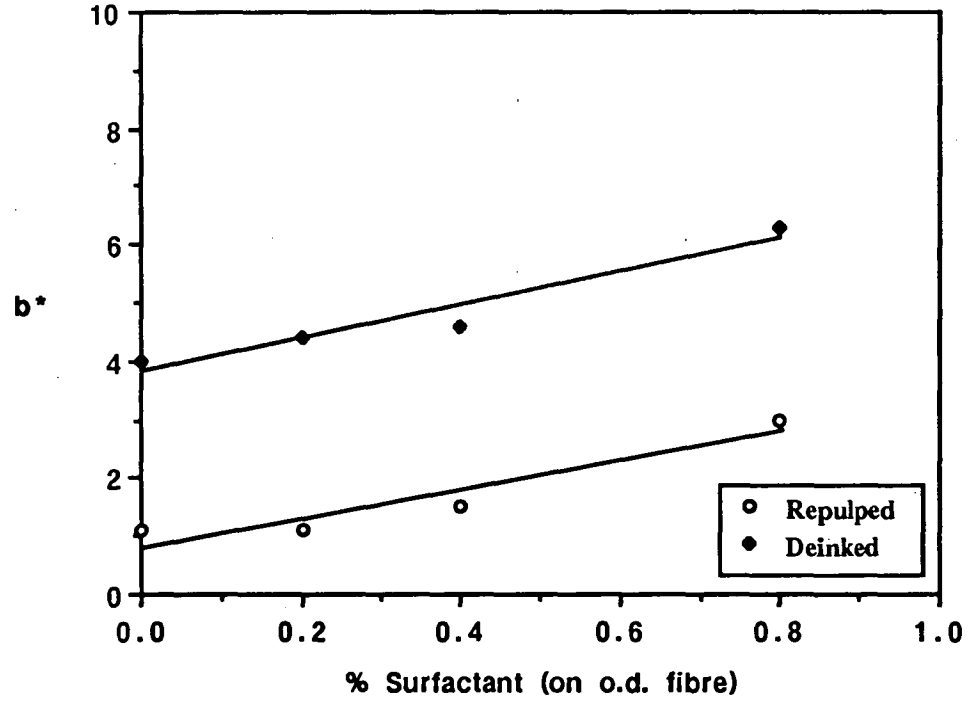

Figure 4.6. Effect of Surfactant B addition (as % o.d. fibre) on b* of pulp after pulping and flotation for deinking of OMG. Pulping and flotation conditions as in Figure 4.4.

Figure 4.4 shows that the brightness responses for the pulp after both pulping and flotation stages increase as the level of surfactant addition increases. This is in contrast to the results for deinking of 100% ONP where brightness loss was observed above a certain level of surfactant addition.

The L* response in Figure 4.5 shows a similar trend as the brightness response. It is interesting to note that, after the pulping stage, the brightness and L* value for 100% OMG is generally lower than those for 100% ONP. However, after the flotation stage, the brightness and L* value for 100% OMG is generally higher than those for 100% ONP (comparing Figure 4.1 to 4.4 and Figure 4.2 to 4.5).

The b* response (Figure 4.6) also shows an increase as the level of surfactant addition increases. Figure 4.6 also shows that the b* values of the pulp after the flotation stage are higher than those after the pulping stage. Comparing Figure 4.6 to 4.3, it was apparent that the b* values for 100% OMG, both after pulping and flotation stage, are generally lower compared to the b* values for 100% ONP.

4.3. Effect of OMG on the deinking of ONP

It is a common practice to use a mixture of newsprint and magazines in industrial deinking processes. A mixture of 70/30 ONP/OMG is common, and this is a typical feedstock composition used at the ANM Albury plant in NSW. It is generally believed that the inorganic fillers introduced with the magazines is beneficial in promoting deinking [1]. It is also widely believed that an ash loading of 8-10% on o.d. fibre needs to be maintained in the flotation cell [2]. However, there are few reported studies of the exact roles which magazine inclusion and filler usage play in the flotation deinking. This section will study the inclusion of OMG in the flotation deinking of ONP and attempt to explain the phenomena observed.

The first part will look at the effect of surfactant addition on the deinking efficiency of 70/30 mixture of ONP/OMG, and the second part will examine the effect of changing the ONP/OMG rates over a wider range.

The effect of surfactant addition on deinking of 70/30 mixture of ONP/OMG on brightness is shown in Figure 4.7. It shows that, for both the pulping and flotation stages, there seems to be an optimum level of addition of surfactant, corresponding to an addition level of ~0.4% on o.d. fibre. Above an addition level of ~0.4% on o.d. fibre, the brightness starts to drop very slightly, though not as noticeable as that observed for the 100% ONP (Figure 4.1).

The L* response in Figure 4.8 shows a similar trend as the brightness response, except that above addition level of ~0.4% on o.d. fibre, the L* appears to remain constant.

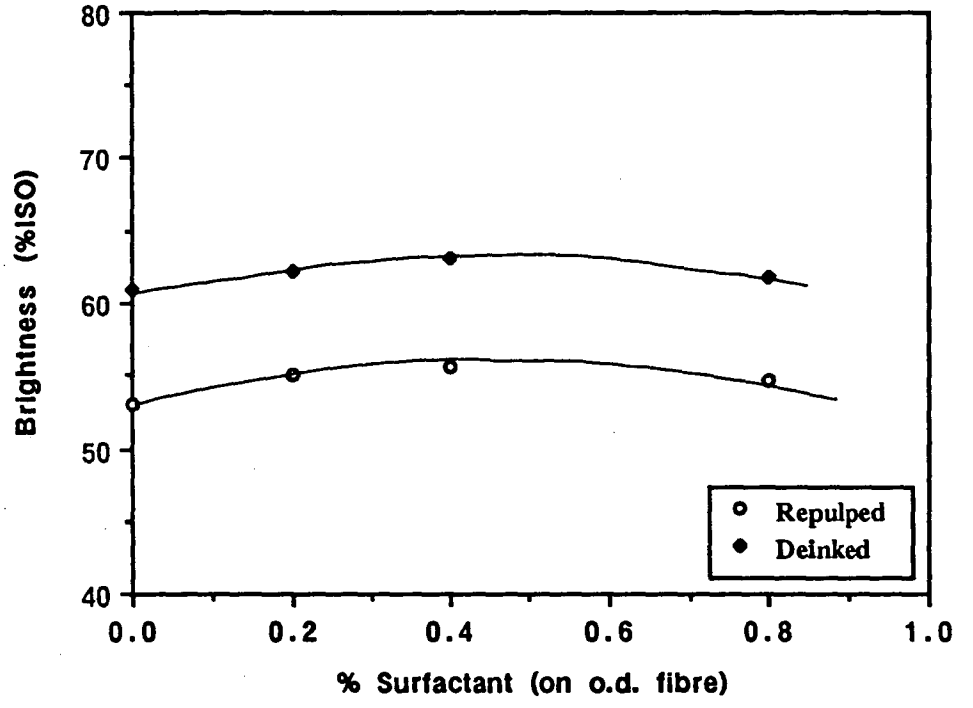

Figure 4.7. Effect of Surfactant B addition (as % o.d. fibre) on brightness of pulp after pulping and flotation for deinking of 70/30 ONP/OMG. Pulping conditions: 1% NaOH, 1% H_2O_2, 1% sodium silicate, 0.2% DTPA; time 20 mins; temperature 50°C; consistency 8%. Flotation conditions: time 6 mins; temperature 50°C; consistency 1%.

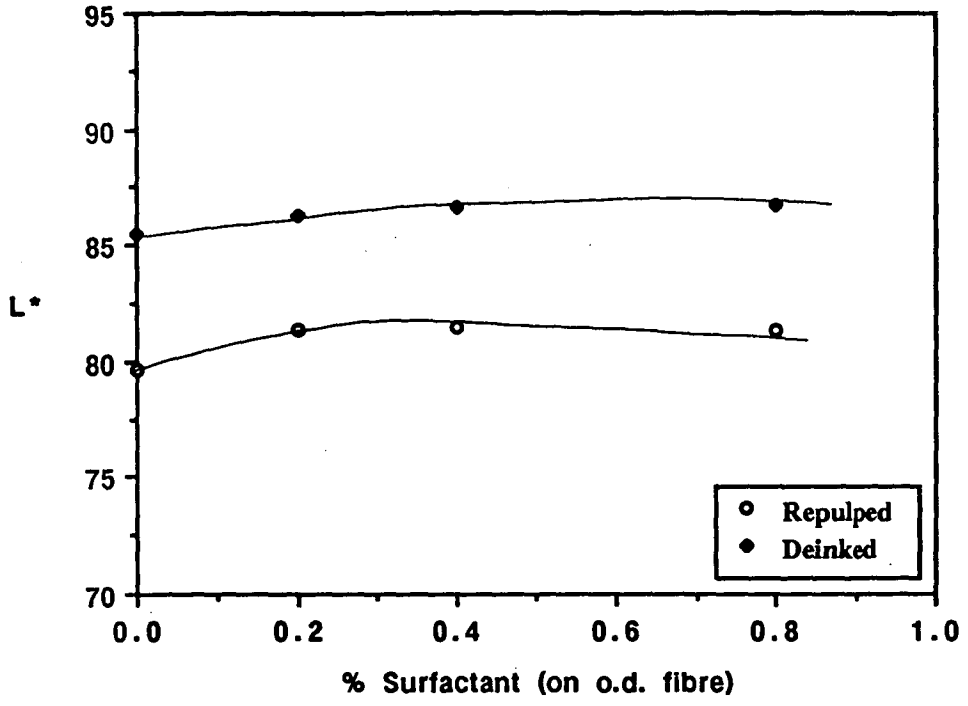

Figure 4.8. Effect of Surfactant B addition (as % o.d. fibre) on b* of pulp after pulping and flotation for deinking of 70/30 ONP/OMG. Pulping and flotation conditions as in Figure 4.7.

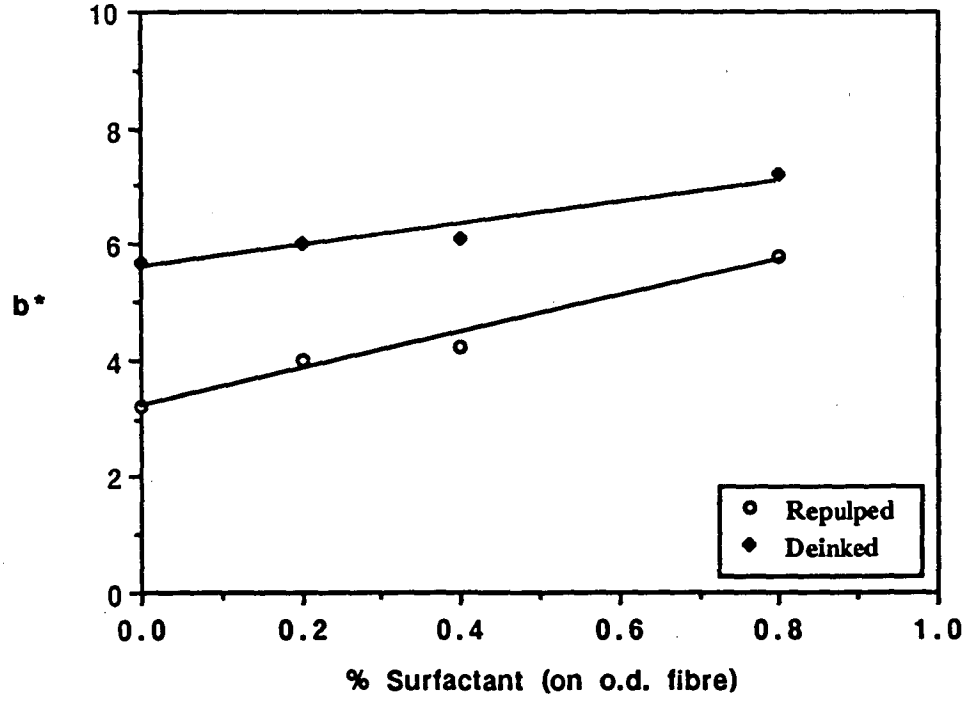

Figure 4.9. Effect of Surfactant B addition (as % o.d. fibre) on b* of pulp after pulping and flotation for deinking of 70/30 ONP/OMG. Pulping and flotation conditions as in Figure 4.7.

The b* response (Figure 4.9) shows an increase as the level of surfactant addition increases. Figure 4.9 also shows that the b* values of the pulp after the flotation stage are higher than those after the pulping stage. Comparing Figure 4.9 to 4.3, it is apparent that the b* values for 70/30 ONP/OMG after the pulping stage are generally lower than the b* values for 100% ONP. However, after the flotation stage, the b* values for 70/30 ONP/OMG are generally comparable to those for 100% ONP.

From the results in Figure 4.7, it seems that the brightness responses of 70/30 mixture of ONP/OMG is a compromise between those of 100% ONP and 100% OMG individually. The brightness for 70/30 mixture of ONP/OMG is not as poor as that for 100% ONP but also not quite as high as that for 100% OMG.

In order to get a deeper insight into the effect of OMG inclusion in flotation deinking of ONP, the experiment over a wider range of rates of OMG inclusion was undertaken. In this experiment, the level of addition of surfactant is fixed at one particular value, i.e. 0.4% on o.d. fibre. Moreover, instead of stopping the flotation experiment after 6 minutes, the duration for flotation time is extended well over an hour with samples being taken at appropriate intervals.

Figure 4.10 shows the effect of OMG inclusion (ranging from 0% through 100% OMG inclusion) on brightness of the pulp over extended flotation time using surfactant B. It can be seen that the rate of brightness increase is highest during the first 10 minutes of flotation. Thereafter only a minor additional brightness increase was observed. In the experiments of flotation of model ink particles done by Larsson et. al. [3], a similar result was reported, where the rate of ink removal is highest during the first 10 minutes.

Figure 4.10 also shows that the highest pulp brightnesses after flotation also correspond to the lowest initial brightnesses after pulping (zero flotation time). In other words, increasing addition of magazines actually causes a decrease in the brightness of the pulp following pulping. This effect has been noted in other studies by Letscher and Sutman [4]. This could be due to a combination of reasons, (i) higher

concentrations of different inks exist in OMG, (ii) lower brightness ONP fibre less affected by ink than higher brightness OMG fibre [5], (iii) much smaller ink particles after pulping in OMG than ONP, where smaller ink particles have a more detrimental effect on brightness [6].

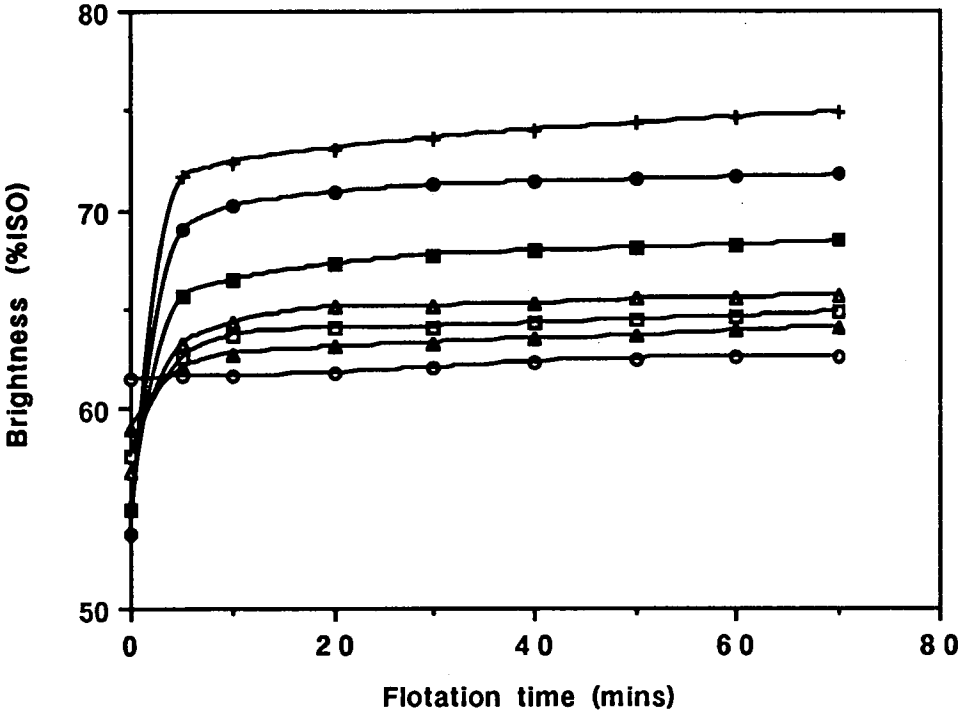

Figure 4.10. Plot of brightness with flotation time for different OMG percentages (ONP makes up the remaining proportion of the furnish) using 0.4% surfactant B. Pulping conditions: 1% NaOH, 1% H_2O_2, 1% sodium silicate, 0.2% DTPA, 0.4% surfactant B; time 20 mins; temperature 50°C; consistency 8%. Flotation conditions: temperature 50°C; consistency 1%, pH 8.5. Magazines (OMG) content :

○ 0% △ 10% □ 20% ▲ 30% ■ 50% ● 80% + 100%

Figure 4.10, which illustrates the correlation between pulp brightness and the proportion of magazines in the feed, shows that addition of OMG increases final brightness throughout the entire range of addition. However, it is not apparent whether this is solely due to the higher brightness from the contribution of the magazine pulp itself, or if the OMG components, such as inorganic fillers and coatings, can also directly influence the deinking of ONP. To assist in answering this question, additional experiments have been undertaken where ONP and OMG were

deinked separately under identical conditions (consistency, temperature, time, chemical additions), after which the resulting pulps were combined in various ratios, designated as 'mixed pulp'. It was prepared so that the mixed pulp had an ONP/OMG ratio the same as the 'actual' pulp, the pulp produced when ONP and OMG are being deinked together. The brightness of the 'mixed pulp' and the 'actual pulp' is plotted in Figure 4.11. Also plotted in Figure 4.11 is calculated brightness for the 'mixed pulp' (designated as theoretical), obtained by taking a weighted average of the brightnesses of pulps from independently deinked ONP and OMG.

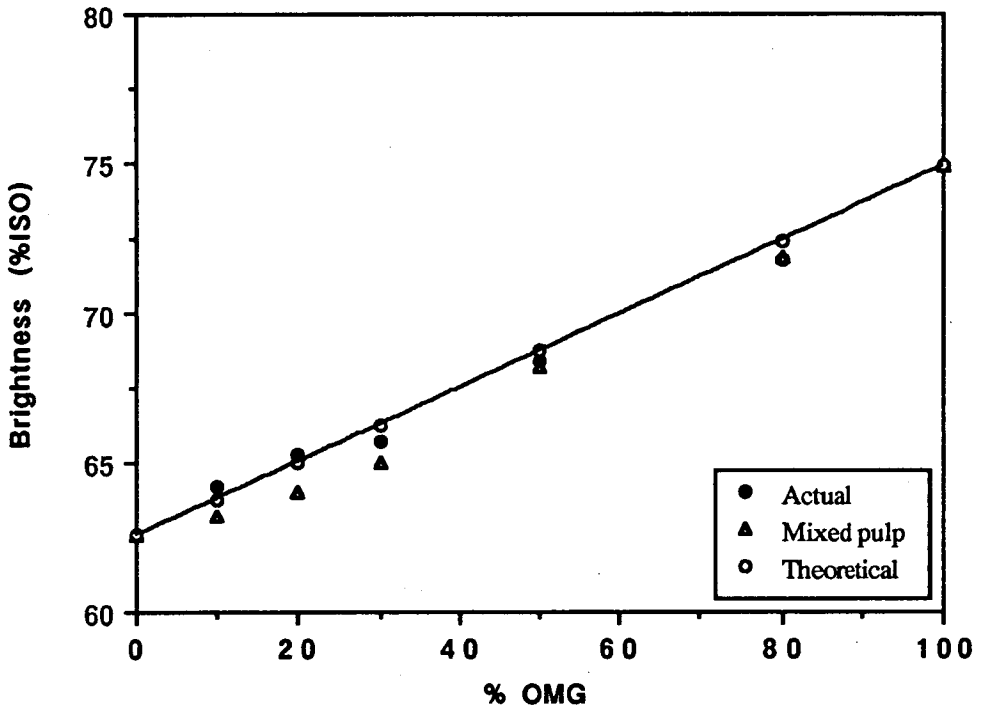

Figure 4.11. Pulp brightness as a function of furnish composition plotted together with corresponding brightnesses for pulp blends prepared from individually deinked ONP and OMG. Calculated values for brightness for blended pulps also shown.

The close correspondence among the three sets of data in Figure 4.11 implies that there is little net interaction between the magazine components and the deinking processes affecting ink removal from ONP. If there was a net interaction between the magazine components and the deinking processes affecting ink removal from ONP, it would be expected that the brightness of the 'actual' pulp would be higher than the

'mixed pulp'. In fact, this is not the case. This confirms the results of the previous study by Letscher and Sutman [4] which reports that addition of OMG to the furnish does not increase the overall efficiency (in terms of brightness) of flotation deinking of ONP.

Benefit of magazine inclusion in the flotation deinking of ONP is that, as OMG typically will have at least 50% bleached kraft fibre, inclusion of OMG in the deinking feedstock can introduce a brighter pulp to the system, hence also contributing to the brightness response. This statement is in agreement with the results in Figure 4.11, where the increase in brightness is proportionally increased with increasing OMG inclusion.

However, it is important to note that foam formation in flotation deinking of 100% ONP is poorer compared to that in flotation deinking of 100% OMG or when there is an inclusion of OMG. In other words, inclusion of OMG in the feedstock contributes to foam formation and/or stability.

4.4. Summary

In flotation deinking of 100% ONP it was observed that too high an addition level of surfactant can have a detrimental effect on the brightness response. For the same range of levels of surfactant addition, this phenomena is not observed in the flotation deinking of 100% OMG.

Inclusion of OMG in the flotation deinking of ONP improves the brightness response over the whole range of rates of OMG inclusion. However, it seems that the higher brightness attained is largely due to the addition of higher brightness materials from the magazines, rather than a more efficient mechanism of ink removal from ONP.

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Chapter 5

Surface Active Agents in Flotation Deinking

5.1. Introduction

Surfactants are surface active materials that contain an organic part that has an affinity for oils (hydrophobe) and another part that has an affinity for the water phase (hydrophile). The hydrophobic group is usually a long chain hydrocarbon while the hydrophilic group is an ionic or, in the case of non-ionic surfactants, a highly polar group. Surfactants are one of the important ingredients in the deinking formulation. They function in deinking systems by lowering the surface tension of water to enable it to wet more effectively and by adsorbing onto surfaces to aid in ink removal and dispersion [1].

Surfactant chemistry and practical applications are complex. Their function and performance are influenced by many application conditions. Commercial surfactants for deinking normally are blends of many components.

The first part of this study of surfactants in flotation deinking presents results of flotation deinking with samples of multi-component surfactant systems. The main components of these surfactants are listed in Table 5.1. The second part will investigate the flotation deinking system using model surfactants, fatty acids of various chain length.

Table 5.1. Multi-component formulation synthetic surfactants (supplied by Buckman Laboratories)

Surfactant sample	Main Components
A	Combination of fatty acids and a non-ionic surfactant.
B	Combination of fatty acid soaps, a non-ionic surfactant, and ethylene glycol.
C	Combination of dimethylamide of C_{18} oil, non-ionic surfactant, anionic surfactant, dipropylene glycol methyl ether, and aromatic solvent.
D	Combination of aromatic hydrocarbon solvent, dipentene, and propylene glycol ethyl ether acetate.

5.2. Multi-component synthetic surfactants

5.2.1. Effects of surfactant addition

The effects of surfactant addition for two of the multi-component surfactants (surfactant samples B and D) on brightness and colour in terms of L*, a*, b* scales were investigated. The feedstock composition used for this study is the 70/30 mixture of ONP and OMG. The percentage of solid yield for these systems is also calculated. It was calculated as follows:

$$\frac{\text{solids added to flotation cell - reject solids}}{\text{solids added to flotation cell}} \times 100$$

The surface tension of the pulping liquor after the pulping stage was also measured.

Figure 5.1 shows the results for the effect of varying the addition level of surfactant sample B on the brightness after pulping and flotation. It shows that above 0.25% addition there is no further significant increase in brightness after flotation. The pulp after pulping also shows similar trends, except brightness continues to increase slightly as the level of surfactant addition increases above 0.25%. The L*

values in Figure 5.2 generally show similar trends as brightness. The b* values in Figure 5.3 after flotation is higher than those after pulping. It again shows very similar trends to brightness and L*.

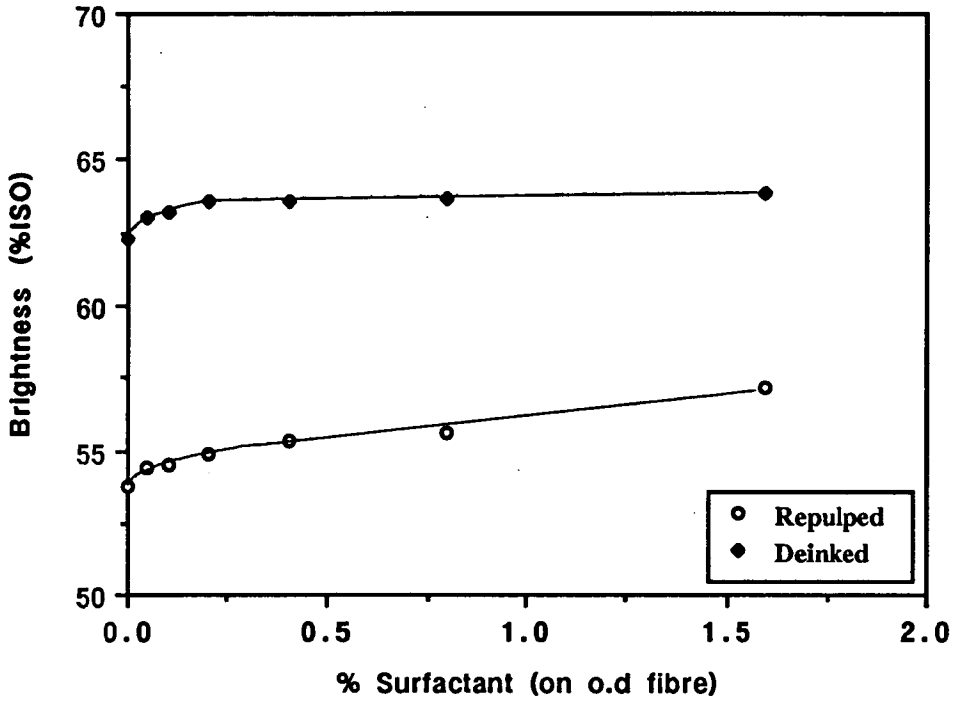

Figure 5.1. Effect of Surfactant B addition (as % o.d. fibre) on brightness of pulp after pulping and flotation for deinking of 70/30 ONP/OMG. Pulping conditions: 1% NaOH, 1% H_2O_2, 1% sodium silicate, 0.2% DTPA; time 20 mins; temperature 50°C; consistency 8%. Flotation conditions: time 6 mins; temperature 50°C; consistency 1%, pH 8.5.

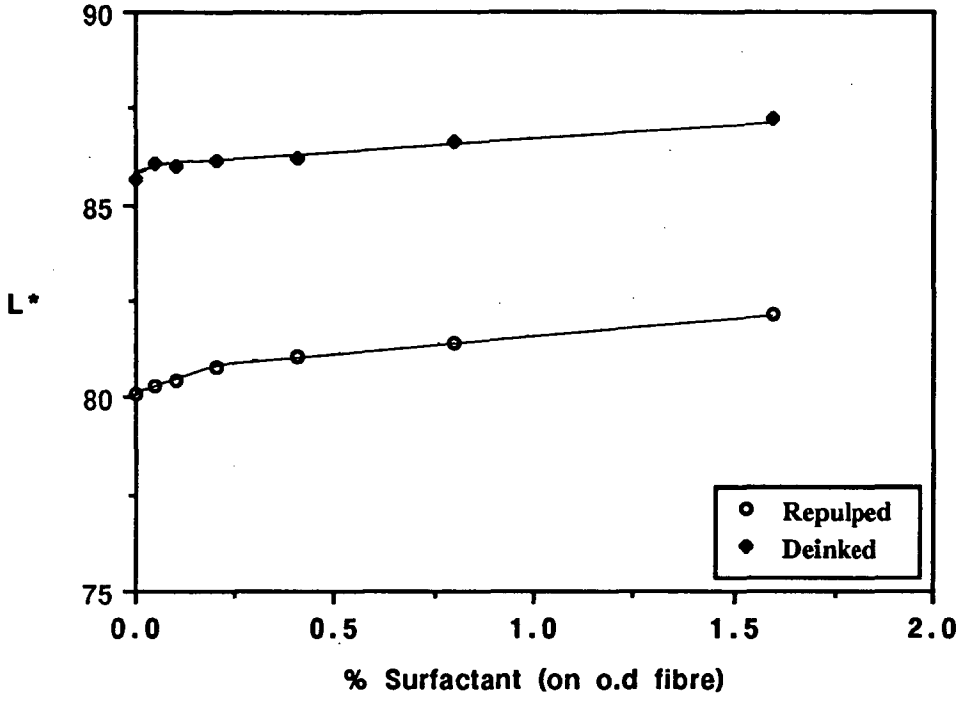

Figure 5.2. Effect of Surfactant B addition (as % o.d. fibre) on L* of pulp after pulping and flotation for deinking of 70/30 ONP/OMG. Pulping and flotation conditions as in Figure 5.1.

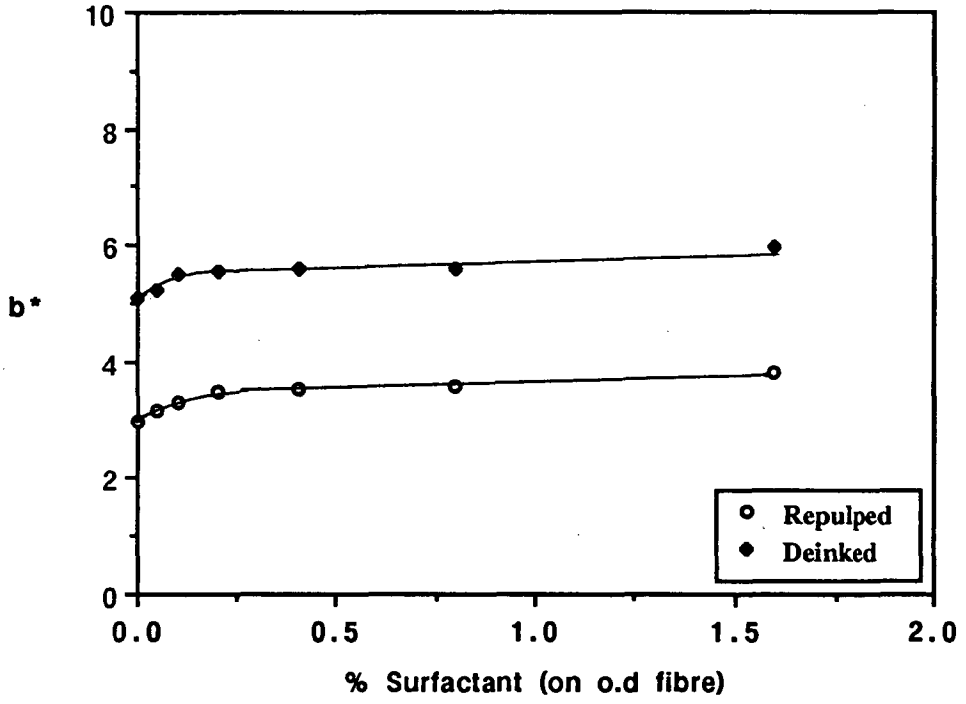

Figure 5.3. Effect of Surfactant B addition (as % o.d. fibre) on b* of pulp after pulping and flotation for deinking of 70/30 ONP/OMG. Pulping and flotation conditions as in Figure 5.1.

Figure 5.4 illustrates the percentage yield of the pulp after flotation. The solid yield decreases at low addition of surfactant with minimum in yield at addition level of 0.25%. The decrease in solid yield corresponds to an increase in fibre, particularly fines, carried over in the flotation stage.

The surface tension measurement of the pulping liquor (Figure 5.5) shows that as the surfactant addition increases the surface tension decreases, as more surfactant molecules align at the liquid-air interface. The surface tension then reaches a stable value after an addition level of 0.25%. This break in the surface tension response is called the critical micelle concentration. At this point, surfactant molecules are forming multi-molecular aggregates called micelles in the bulk of the solution instead of increasingly packing the surface of the liquid. The critical micelle concentration (cmc) of the surfactant sample B occurs at the addition level of 0.25%. This corresponds to the minimum in solid yield (Figure 5.4) and also to the point of levelling off in brightness response (Figure 5.1).

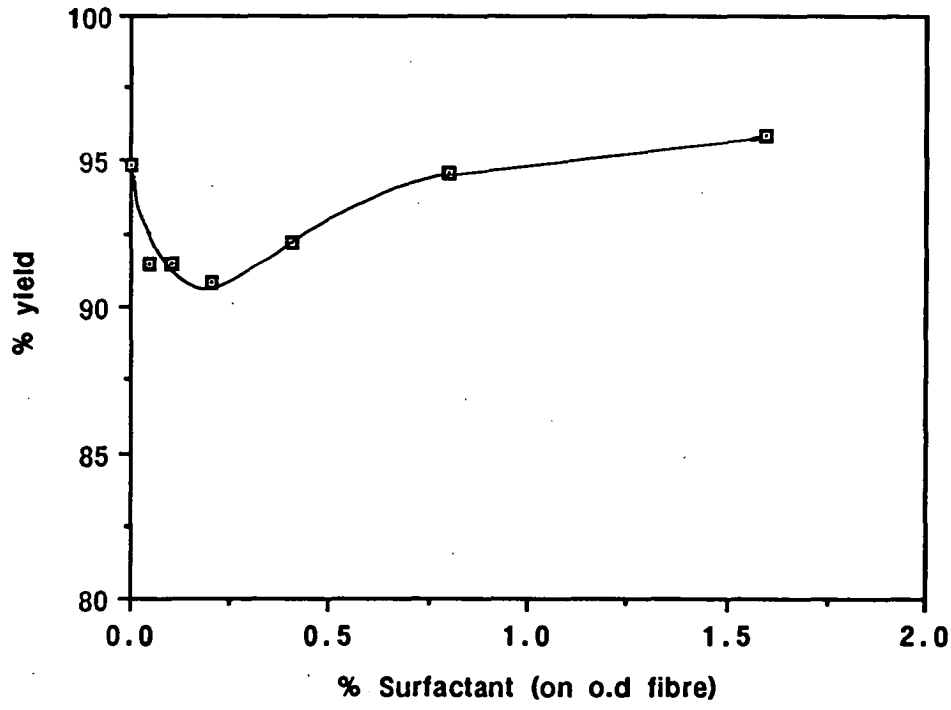

Figure 5.4. Effect of Surfactant B addition (as % o.d. fibre) on % yield of solid after flotation for deinking of 70/30 ONP/OMG. Pulping and flotation conditions as in Figure 5.1.

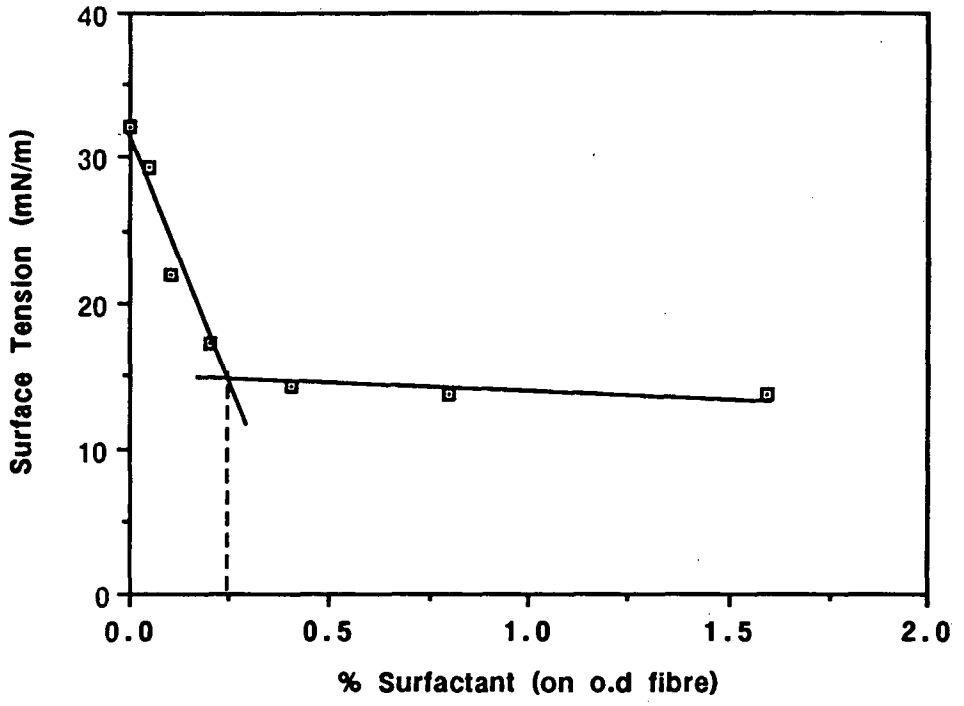

Figure 5.5. Effect of Surfactant B addition (as % o.d. fibre) on surface tension of the pulping liquor in deinking of 70/30 ONP/OMG. Pulping conditions as in Figure 5.1.

Figure 5.6 shows the results for the effect of varying the addition level of surfactant sample D on the brightness after pulping and flotation. It shows an initial increase then decrease. The L* values, in Figure 5.7, generally show similar trends to brightness. The b* values, in Figure 5.8, after flotation are higher than those after pulping. It again shows very similar trends to brightness and L*.

Figure 5.9 illustrates the percentage of yield of the pulp after flotation. The solid yield decreases at low addition of surfactant with minimum in yield at addition level of 0.4%. The surface tension measurement of the pulping liquor (Figure 5.10) shows that as the surfactant addition increases the surface tension decreases, as more surfactant molecules align at the liquid-air interface. The surface tension then reaches a stable value after addition level of 0.4%. Thus, the critical micelle concentration (cmc) of the surfactant sample D occurs at the addition level of 0.4%. This corresponds to the minimum in solid yield (Figure 5.9) but in the case of brightness (Figure 5.6), the maximum occurs at a much lower addition level than the cmc.

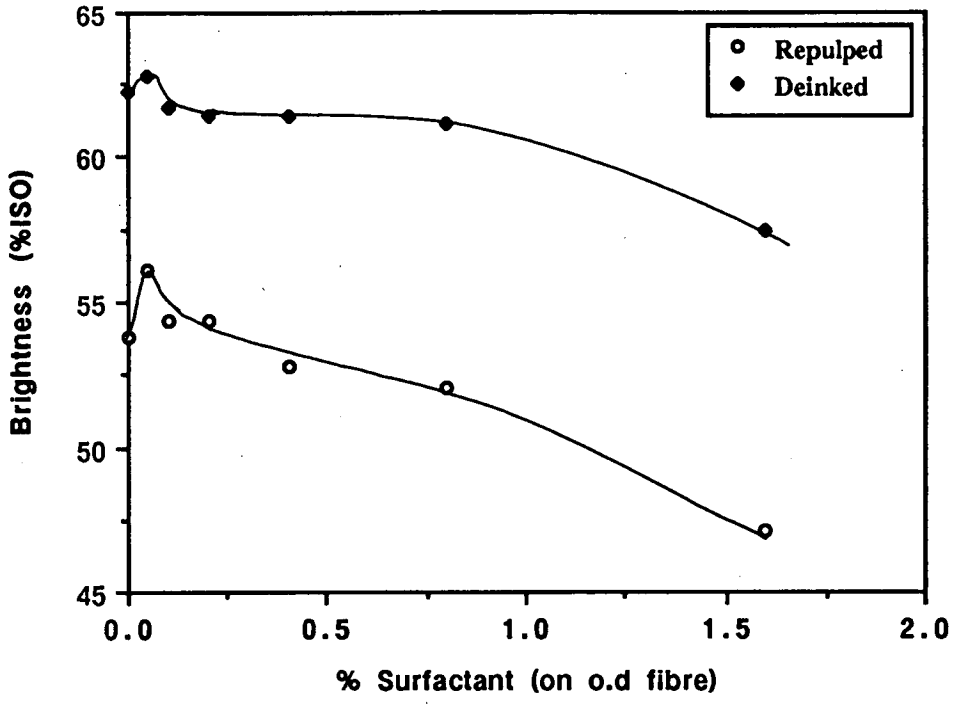

Figure 5.6. Effect of Surfactant D addition (as % o.d. fibre) on brightness of pulp after pulping and flotation for deinking of 70/30 ONP/OMG. Pulping conditions: 1% NaOH, 1% H_2O_2, 1% sodium silicate, 0.2% DTPA; time 20 mins; temperature 50°C; consistency 8%. Flotation conditions: time 6 mins; temperature 50°C; consistency 1%, pH 8.5.

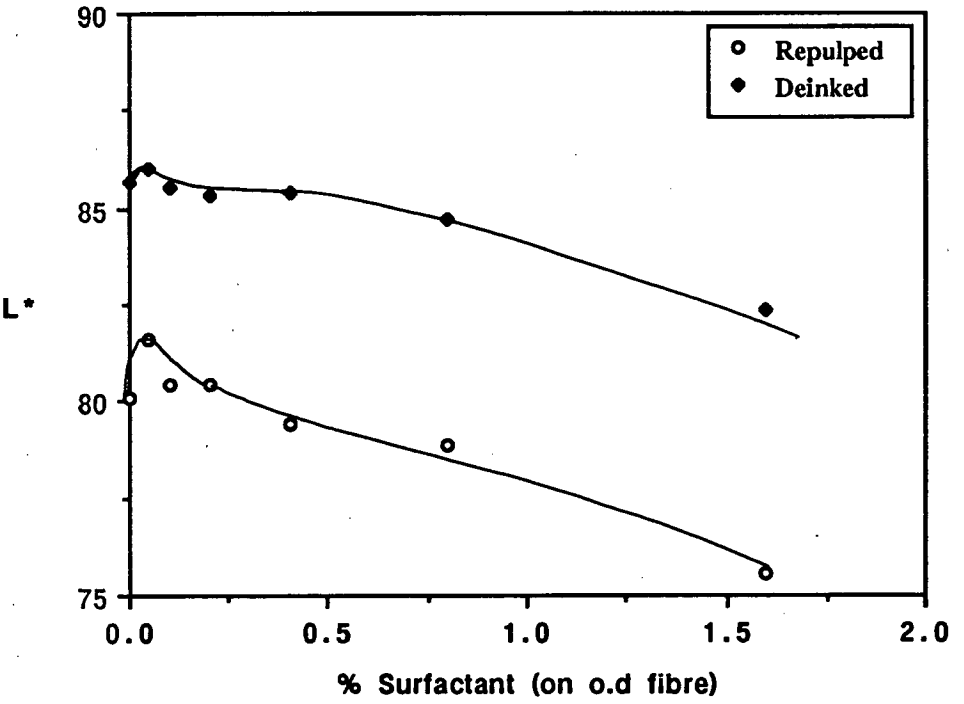

Figure 5.7. Effect of Surfactant D addition (as % o.d. fibre) on L* of pulp after pulping and flotation for deinking of 70/30 ONP/OMG. Pulping and flotation conditions as in Figure 5.10.

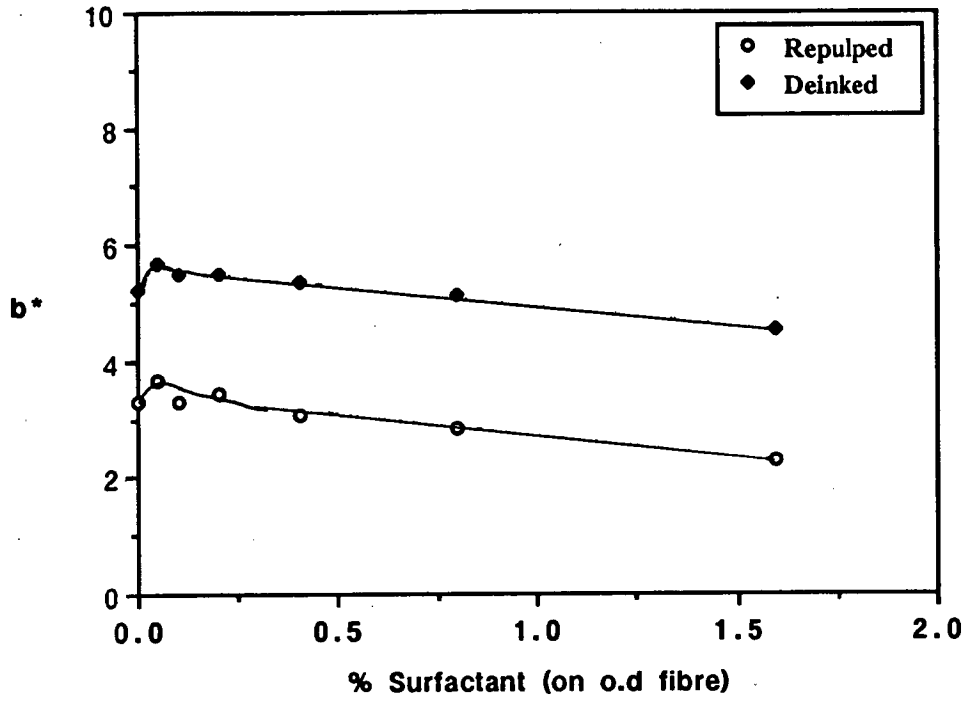

Figure 5.8. Effect of Surfactant D addition (as % o.d. fibre) on b* of pulp after pulping and flotation for deinking of 70/30 ONP/OMG. Pulping and flotation conditions as in Figure 5.10.

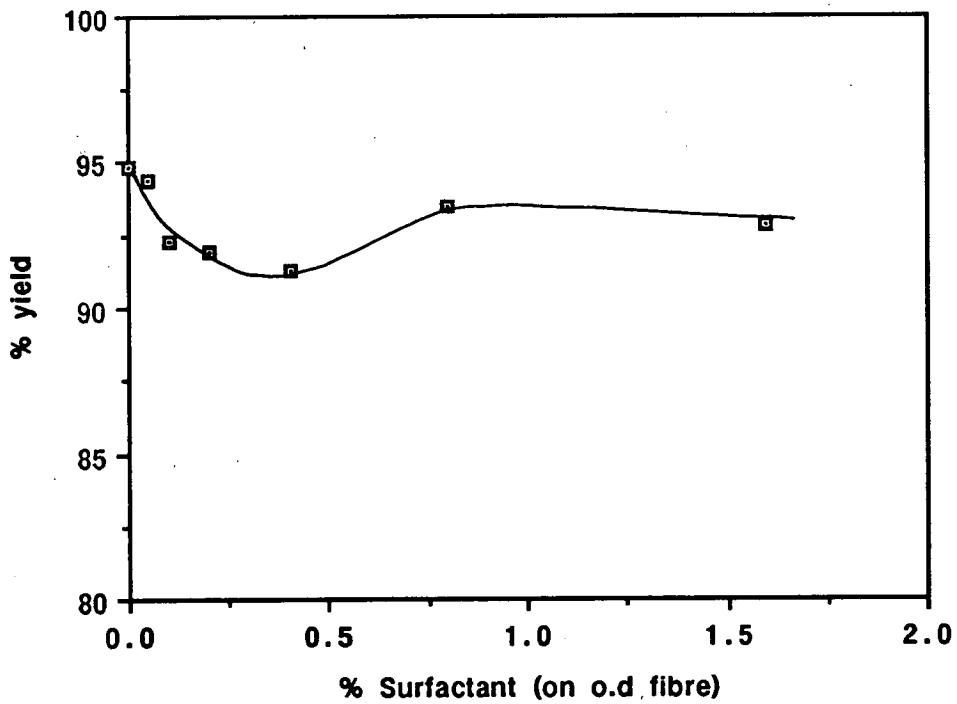

Figure 5.9. Effect of Surfactant D addition (as % o.d. fibre) on % yield of solid after flotation for deinking of 70/30 ONP/OMG. Pulping and flotation conditions as in Figure 5.10.

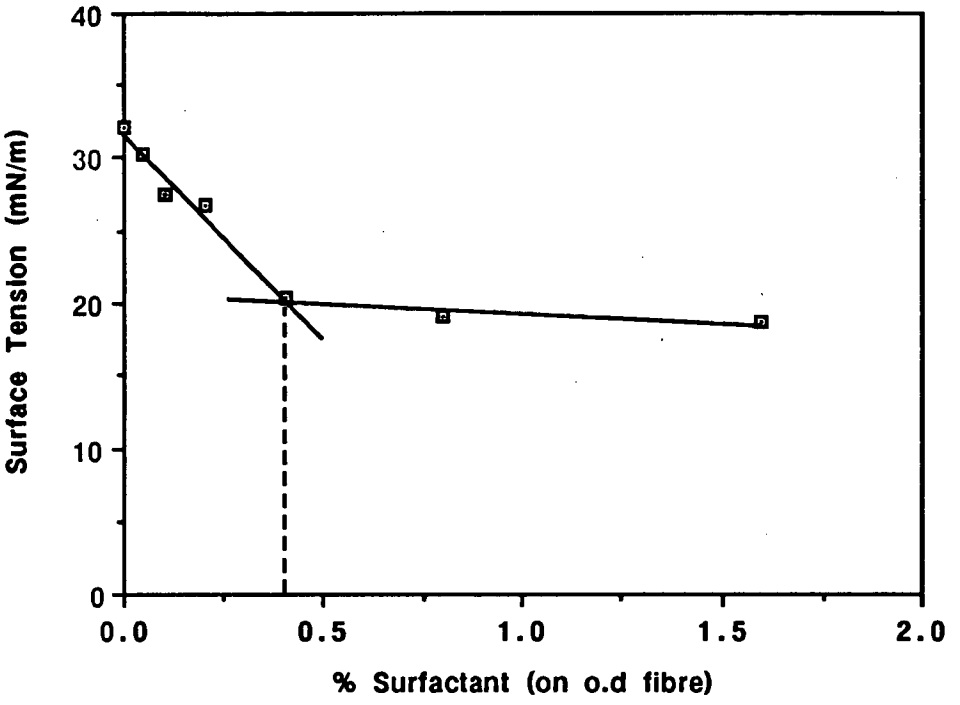

Figure 5.10. Effect of Surfactant D addition (as % o.d. fibre) on surface tension of the pulping liquor in deinking of 70/30 ONP/OMG. Pulping conditions as in Figure 5.10.

5.2.2. Effects of pH

The effects of flotation pH on brightness for three multi-component surfactants were investigated. The results are shown in Figure 5.11. For surfactants A and B, there is clearly an optimum flotation pH level at ~8.5. For surfactant C, the variation in pH level does not have a significant effect on final brightness attained over the pH range 2 - 9.

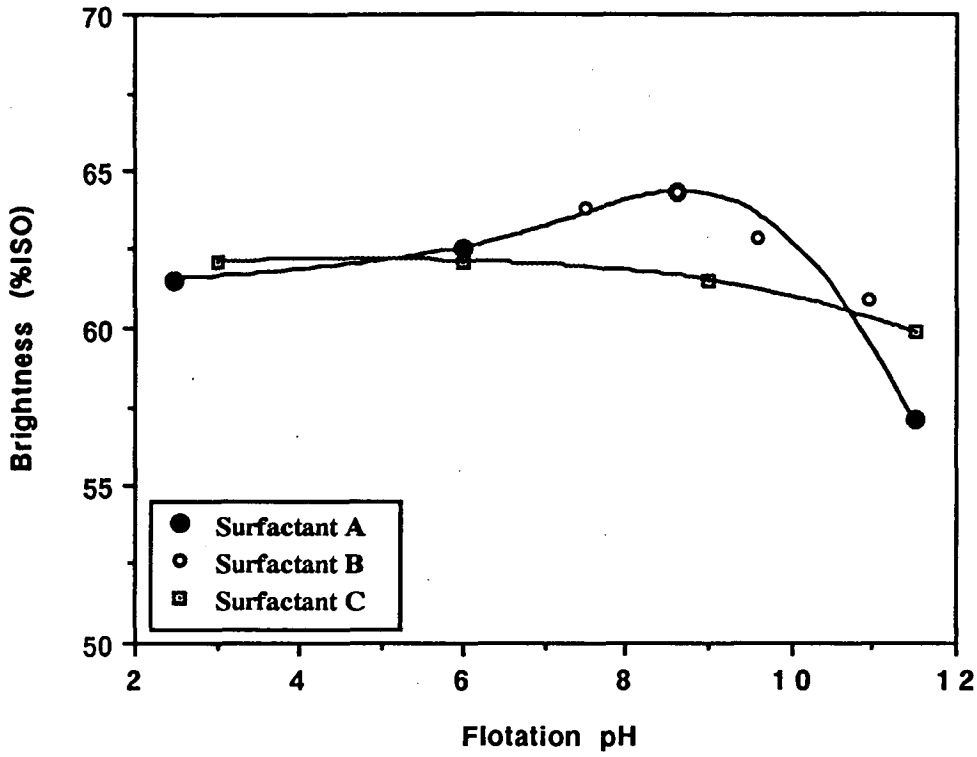

Figure 5.11. Effect of pH adjustment prior to flotation stage on the final brightness for deinking of 70/30 mixture of ONP/OMG. Pulping conditions: 1% H_2O_2, 1% NaOH, 1% sodium silicate, 0.2% DTPA, 0.4% deinking surfactant; time 20 mins; temperature 50°C; consistency 8%.

Results on the ink speck evaluation of the deinked pulps are shown in Figure 5.12. It shows that, for surfactant sample A, an increase in speck count was observed above pH 8.5. For deinking surfactant sample C, the speck count response generally decreased as the pH increased over the range studied. These results suggest that the decrease in the brightness response above pH 8.5 is not only due to alkali yellowing but can also be due to the increasing ink speck count, which probably is due to the re-deposition of ink particles onto the fibre. Hence, the performance of the surfactants themselves in removing ink particles from the pulp slurry in the flotation stage is affected by pH. The difference in behaviour between surfactants A and C may be associated with their chemical composition. Table 5.1 shows that surfactant A consists primarily of fatty acids, whilst surfactant C predominantly consists of dimethylamide of C_{18} oils.

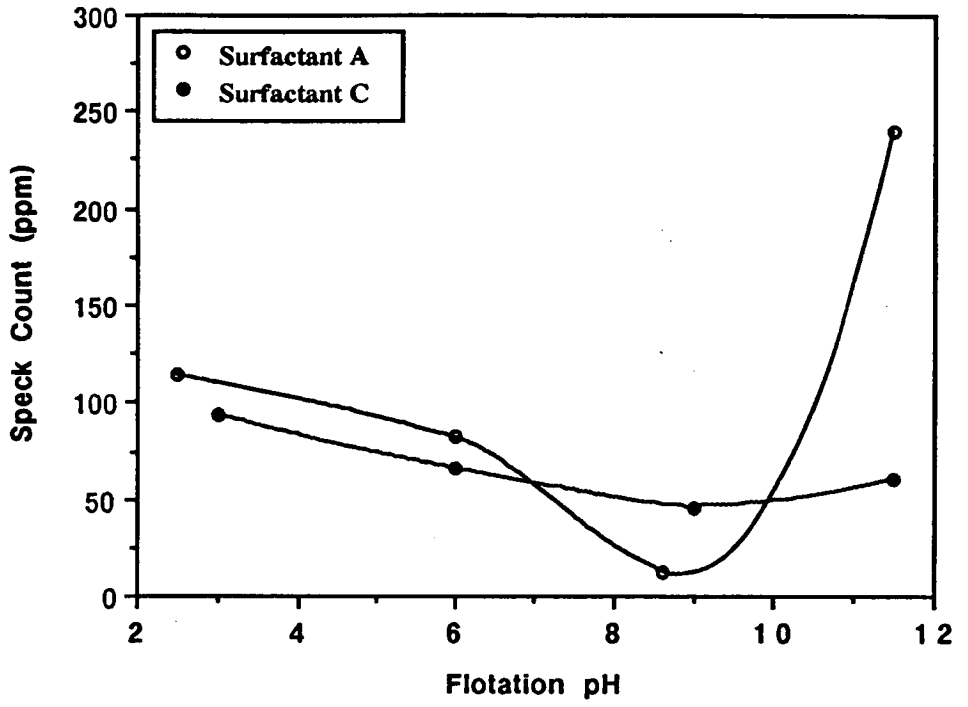

Figure 5.12. Effect of pH adjustment prior to flotation stage on the speck count for deinking of 70/30 mixture of ONP/OMG. Pulping and flotation conditions as in Figure 5.11.

5.3. Model fatty acid surfactants

5.3.1. Effects of chain length

From Table 5.1, it is evident that fatty acid is one of the main components in the multi-component surfactants studied. Therefore, it was decided to investigate the performance of fatty acids in flotation deinking. The first part was to investigate the effect of chain length in fatty acids on deinking efficiency in terms of brightness, L* and b*. Linear fatty acids with numbers of carbon atoms ranging from 12 to 20 were chosen for this study. The addition level of each was kept constant on a molar basis, i.e. 5.27 mmole fatty acid, corresponding to an addition level of 0.2% stearic acid (C_{18} fatty acid).

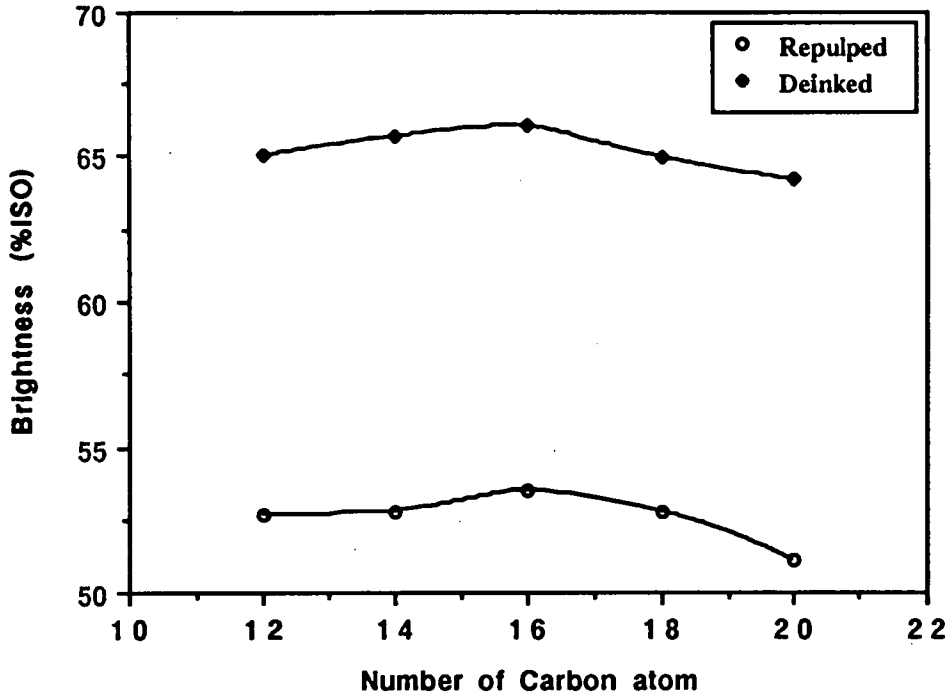

Figure 5.13. Effect of chain length of the fatty acid on brightness of pulp after pulping and flotation for deinking of 70/30 ONP/OMG. Pulping conditions: 1% NaOH, 1% H_2O_2, 1% sodium silicate, 0.2% DTPA, 5.27 mmole fatty acid; time 20 mins; temperature 50°C; consistency 8%. Flotation conditions: time 6 mins; temperature 50°C; consistency 1%.

Under the pulping and flotation conditions performed in this study, it was found that generally there is little effect of chain length on brightness (Figure 5.13). There is a small improvement in brightness response at C_{16} after both pulping and flotation. The response on L* (Figure 5.14) and b* (Figure 5.15) shows similar trends to that on brightness.

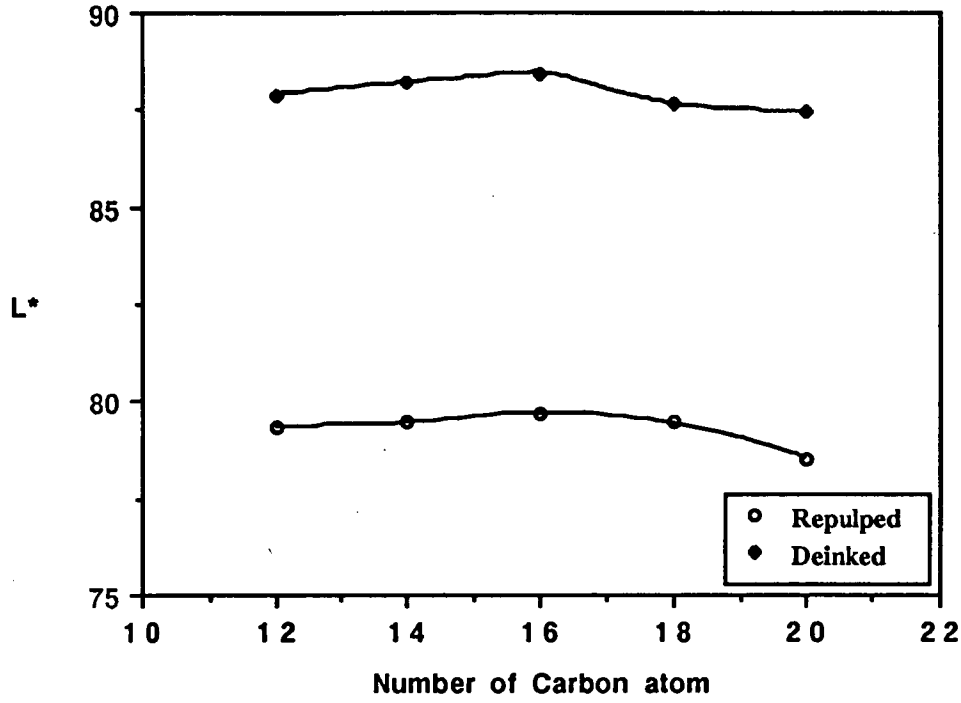

Figure 5.14. Effect of chain length of the fatty acid on L* of pulp after pulping and flotation for deinking of 70/30 ONP/OMG. Pulping and flotation conditions as in Figure 5.13.

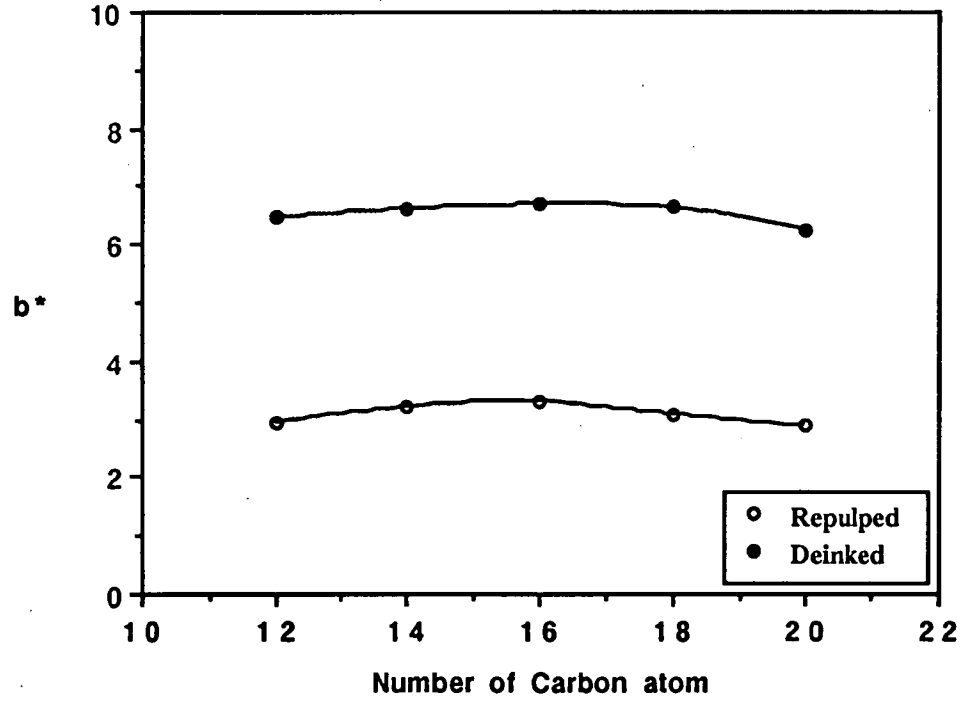

Figure 5.15. Effect of chain length of the fatty acid on b* of pulp after pulping and flotation for deinking of 70/30 ONP/OMG. Pulping and flotation conditions as in Figure 5.13.

Figure 5.16 shows the brightness response for deinking with 0.2% (5.27 mmole) stearic acid for different feedstock compositions. It illustrates that the brightness response improves as %OMG increases. This can be due to either the higher brightness of magazines or improved deinking as feedstock composition changes. This response shows very similar trends to the previous experiment using a multi-component surfactant sample B (in Figure 4.10).

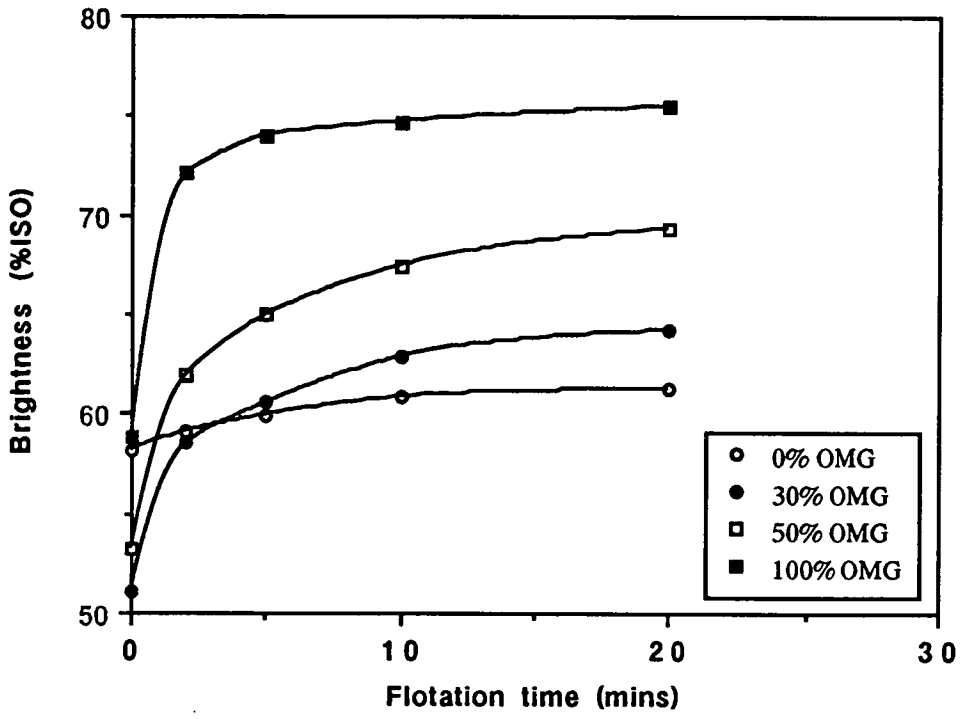

Figure 5.16. Plot of brightness with flotation time for different OMG percentages (ONP makes up the remaining proportion of the furnish) using 0.2% (on o.d. fibre) stearic acid. Pulping conditions: 1% NaOH, 1% H_2O_2, 1% sodium silicate, 0.2% DTPA, 5.27 mmole stearic acid; time 20 mins; temperature 50°C; consistency 8%. Flotation conditions: temperature 50°C; consistency 1%.

Figure 5.17 shows the correlation of the proportion of magazines in the feed to the final brightness as well as to the water hardness of the liquor after pulping stage. It is apparent that addition of magazines increases the final brightness as well as the water hardness throughout the entire range of addition.

The increase in the water hardness with increasing proportion of magazines in the deinking feedstock is largely due to the calcium carbonate in magazines being released into solution. Results of analysis of ash contents in the magazines samples,

as shown in Table 5.2, reveals that calcium is one of the main components in the ash of the OMG sample.

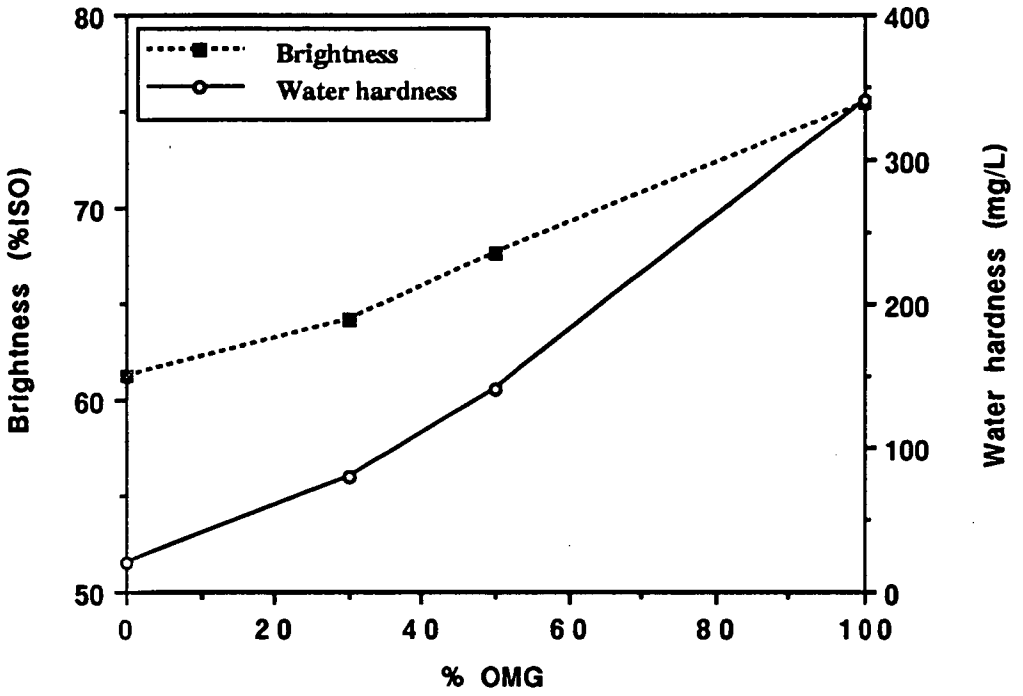

Figure 5.17. Correlation of pulp brightness and water hardness of the pulping liquor to the proportion of magazines (OMG) in the feedstock. Pulping and flotation conditions as in Figure 5.16.

Table 5.2. Analysis results of major components in the ash of coated magazines (Total ash content of 26% w/w)

Compound	Concentration (% w/w)
SiO_2	35.44
Al_2O_3	27.42
CaO	20.74

5.3.2. Effects of addition of Ca^{2+} in pulping stage

This section will study in more detail the role of Ca^{2+} in flotation deinking using fatty acids. It was indicated in the previous section that calcium ions which come from the magazine paper might affect the deinking efficiency. The system with

and without the fatty acid (Lauric Acid, C_{12}) is treated with addition of small amounts of Ca^{2+} (added as $CaCl_2$). The results are shown in Figures 5.18 to 5.20. The brightness response for the system without fatty acid shows that addition of 0.1% (8.3 mmole) Ca^{2+} had a slightly detrimental effect (Figure 5.18). With the system with 5.27 mmole Lauric acid, the addition of 0.1% (8.3 mmole) Ca^{2+} has a slightly beneficial effect on brightness (Figure 5.18). It is interesting to note that the brightness of the pulp after pulping (i.e. at zero flotation time) for the systems with 0.1% (8.3 mmole) Ca^{2+} is lower compared to that without addition of calcium.

The response of the L* value (Figure 5.19) generally shows similar trends to that of brightness. For the b* value response (Figure 5.20), it is apparent that for the system without fatty acid the b* value with calcium addition is higher than that without calcium addition.

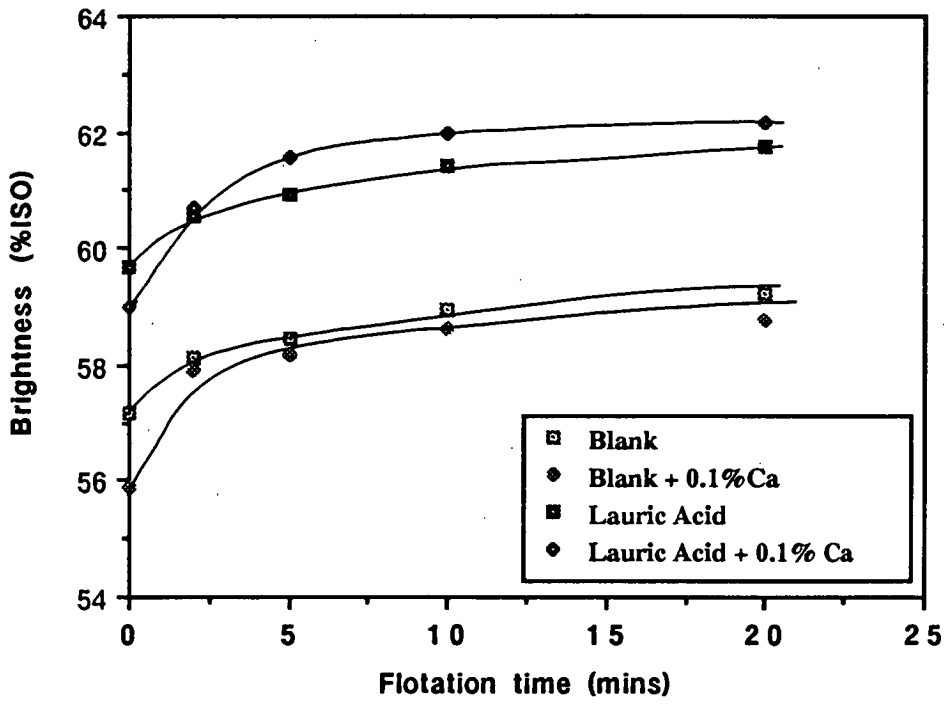

Figure 5.18. Effect of addition of Ca^{2+} ion (addition of 0.1% on o.d. fibre Ca^{2+} or equivalent to 8.3 mmol Ca^{2+}) in the pulping stage on brightness for flotation deinking of 100% ONP with and without 5.27 mmole lauric acid. Pulping conditions: 1% NaOH, 1% H_2O_2, 1% sodium silicate, 0.2% DTPA; time 20 mins; temperature 50°C; consistency 8%. Flotation conditions: temperature 50°C; consistency 1%.

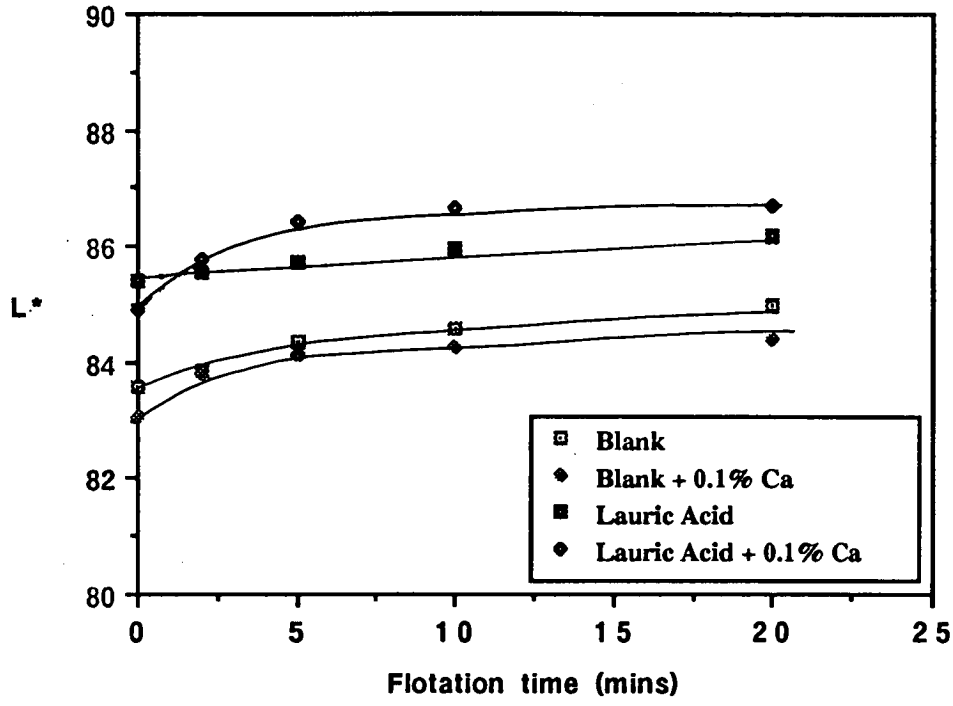

Figure 5.19. Effect of addition of Ca^{2+} ion (addition of 0.1% on o.d. fibre Ca^{2+} or equivalent to 8.3 mmol Ca^{2+}) in the pulping stage on L* for flotation deinking of 100% ONP with and without 5.27 mmole lauric acid. Pulping and flotation conditions as in Figure 5.18.

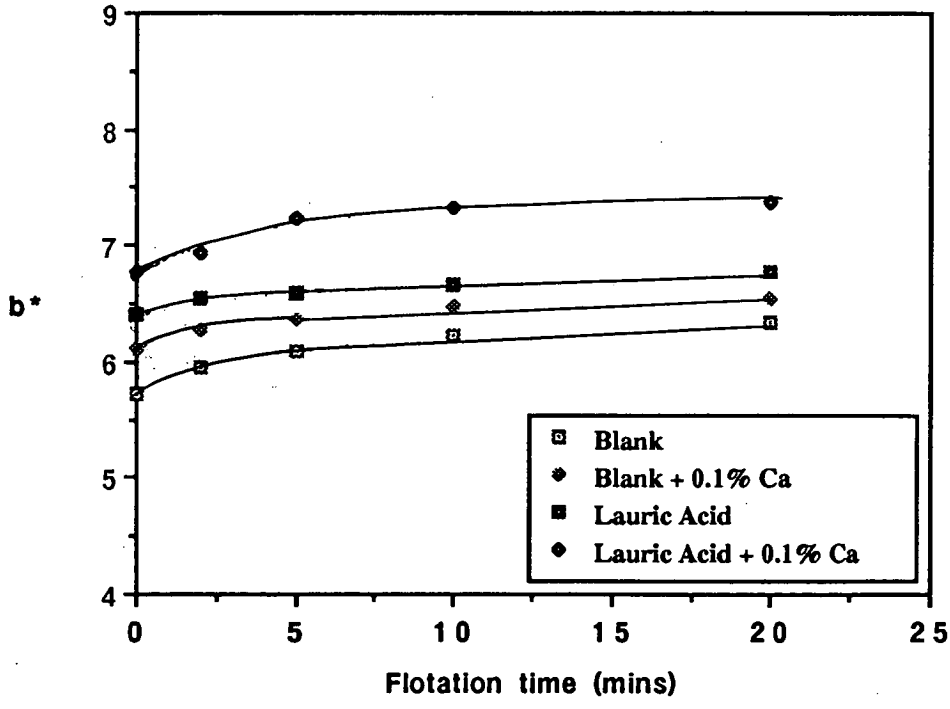

Figure 5.20. Effect of addition of Ca^{2+} ion (addition of 0.1% on o.d. fibre Ca^{2+} or equivalent to 8.3 mmol Ca^{2+}) in the pulping stage on b* for flotation deinking of 100% ONP with and without 5.27 mmole lauric acid. Pulping and flotation conditions as in Figure 5.18.

It is illustrated in Figure 5.17 that the increase in %OMG in feedstock composition also increases the water hardness, hence most likely the concentration of calcium ion. It was also apparent that the increase in %OMG increases the brightness response. Therefore, it is interesting to see whether the increase in the water hardness, or in other words the increase in the concentration of Ca^{2+} ion, by itself can improve the final brightness for the deinking of 100% ONP. By adding Ca^{2+} ion during the pulping stage (added as $CaCl_2$), the water hardness of the pulping liquor can be adjusted.

Figures 5.21 to 5.23 show the effect of Ca^{2+} addition and corresponding water hardness on brightness, L* and b*, respectively. The results in Figures 5.21 to 5.23 seem to suggest that, for flotation deinking of ONP, there is an optimum level of Ca^{2+} needed, corresponding to addition of 10 mmol Ca^{2+} or water hardness of 50 mg/L. Large excesses of Ca^{2+} have detrimental effects.

In the flotation model proposed by Larsson et.al. [2], the ink particles obtained a negative charge due to the small amount of organic acids in the ink. The acids are enriched in the surface layer and become ionised under alkaline conditions. When soap is added it will to a great extent adsorb on the ink particles and make their charge even more negative. The high negative charge on the ink particles gives them an electrostatic stabilisation, which is favourable for the release of ink from the fibres. On the other hand, the charge efficiently prevents them from attaching to air bubbles and must therefore be eliminated before the flotation stage. This is when calcium ions become beneficial by precipitating the soap, counter-balancing the negative charge, and making the ink particles more hydrophobic.

From the flotation model above, it is understandable why there is an optimum level of Ca^{2+} in the pulping stage, as shown in Figure 5.21. Its concentration should be high enough to promote hydrophobicity in the flotation stage, but not too high such that it interferes with the separation of ink particles from the fibres in the pulping stage.

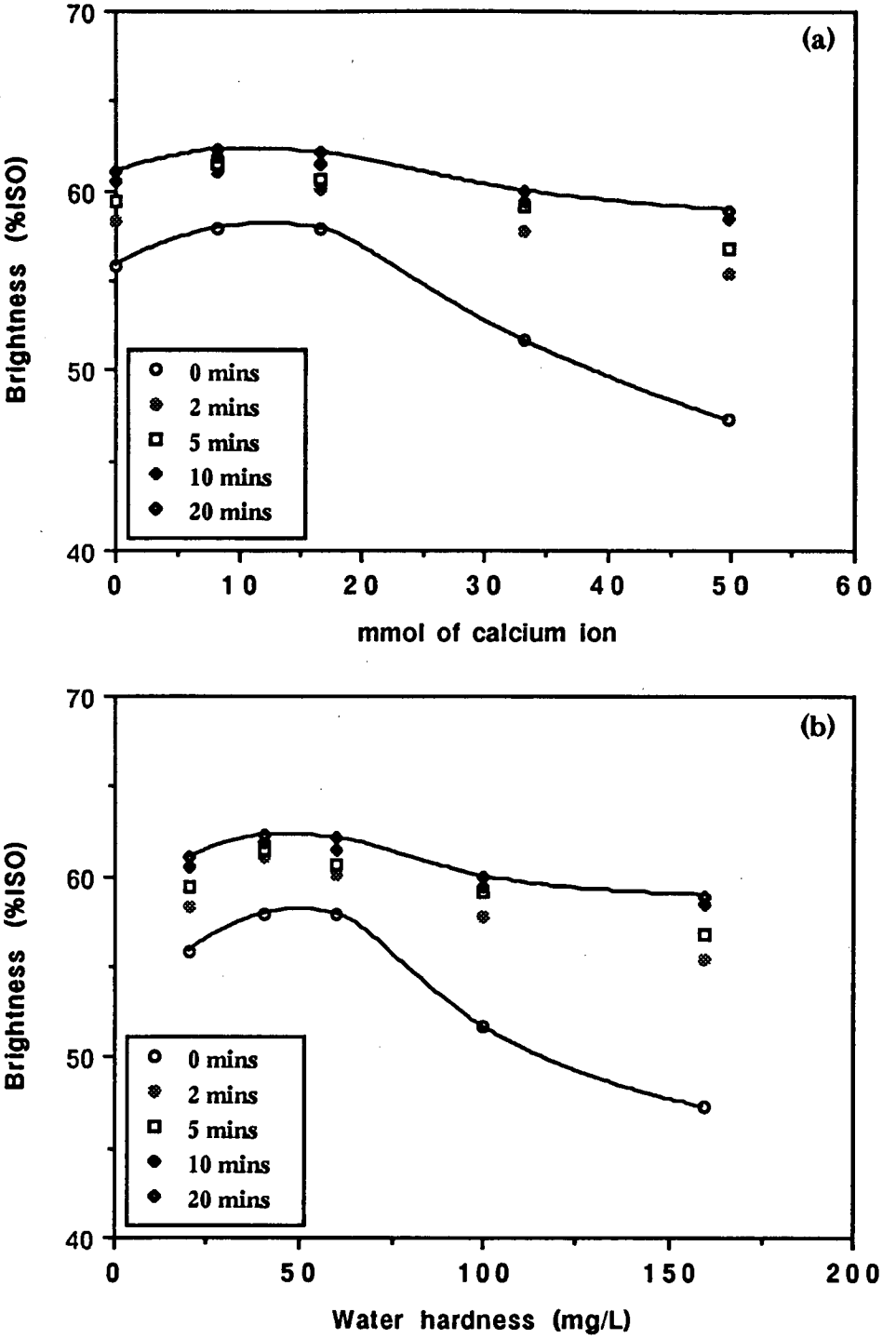

Figure 5.21. Plot of brightness against (a) mmol of Ca^{2+} added to the system and (b) resulting water hardness of the pulping liquor for flotation deinking of 100% ONP with 0.2% stearic acid. Pulping conditions: 1% NaOH, 1% H_2O_2, 1% sodium silicate, 0.2% DTPA, 0.2% stearic acid; time 20 mins; temperature 50°C; consistency 8%. Flotation conditions: temperature 50°C; consistency 1%.

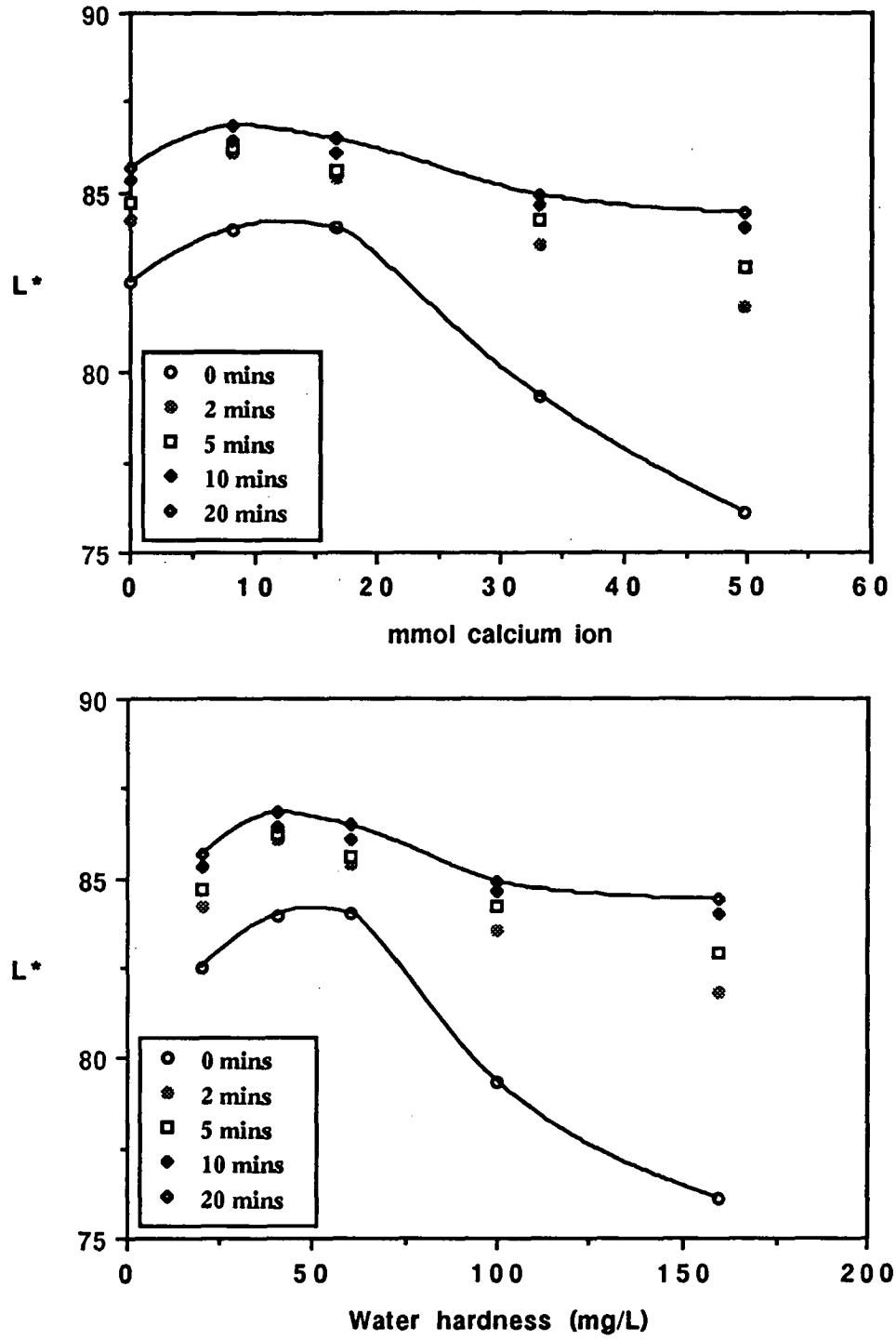

Figure 5.22. Plot of L* against (a) mmol of Ca^{2+} added to the system and (b) resulting water hardness of the pulping liquor for flotation deinking of 100% ONP with 0.2% stearic acid. Pulping and flotation conditions as in Figure 5.21.

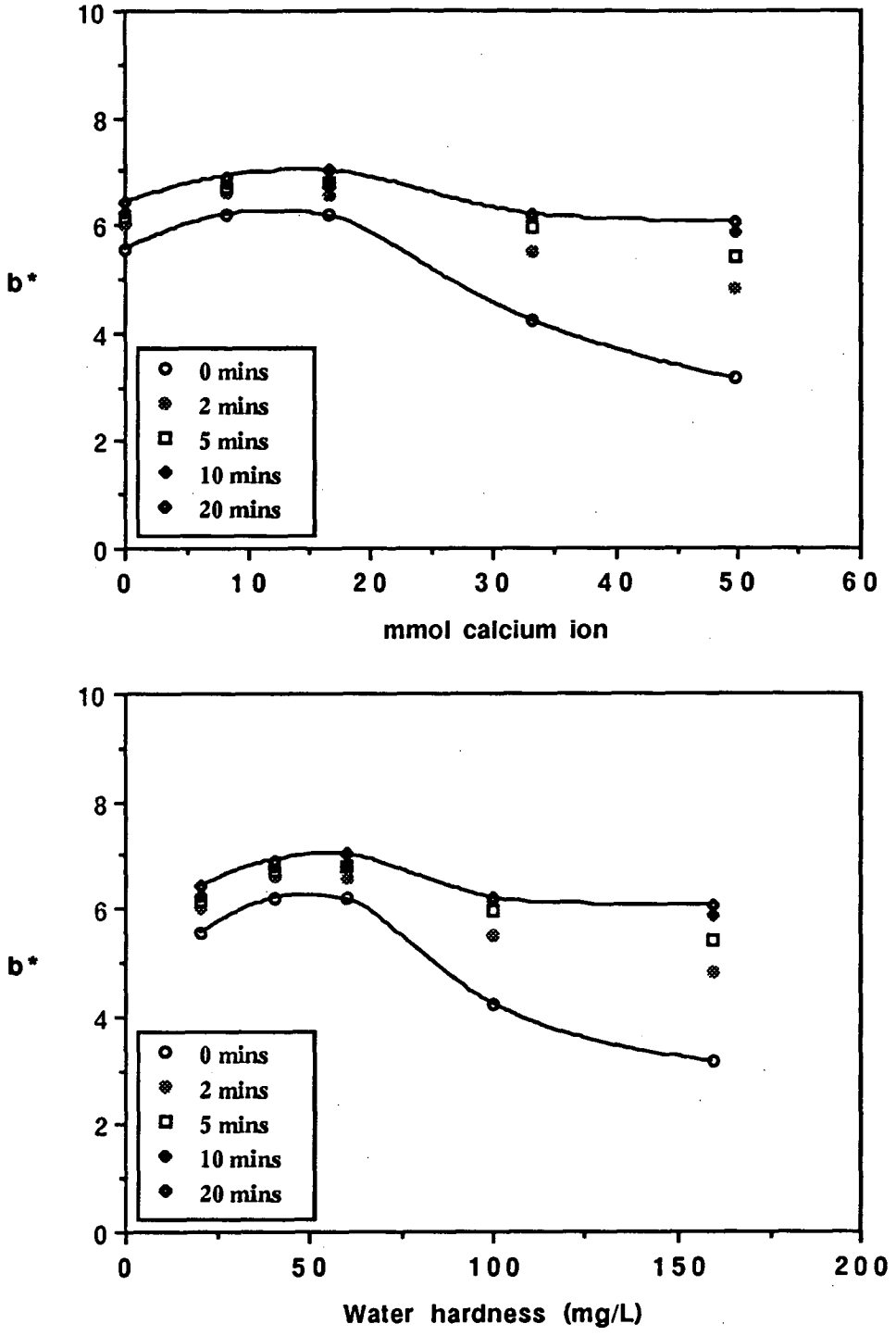

Figure 5.23. Plot of b* against (a) mmol of Ca^{2+} added to the system and (b) resulting water hardness of the pulping liquor for flotation deinking of 100% ONP with 0.2% stearic acid. Pulping and flotation conditions as in Figure 5.21.

Comparing the results in Figure 5.21 with those in Figure 5.17, it is apparent that a higher brightness occurs at much higher levels of water hardness than appear

optimum for this surfactant. This suggests that factors other than the level of water hardness (concentration of Ca^{2+} ion) are more important in determining the final brightness attained for deinking of a mixture of ONP and OMG. In other words, improvement in brightness response in the deinking of offset printed newsprint (ONP) by addition of coated magazines (OMG) is not due to the higher level of Ca^{2+} derived from the inorganic filler in the OMG.

5.4. Summary

The two multi-component surfactants studied behaved differently. The existence of an optimum level of addition of surfactant was apparent, corresponding to an addition level of 0.25% for surfactant B and 0.1% for surfactant D. It was observed that solid yield generally decreased with increasing addition level of surfactant up to a minimum, which seems to correspond to the critical micelle concentration (cmc) of the surfactants.

Flotation pH affects the performance of multi-component surfactant A, which consists primarily of fatty acids. High flotation pH has a negative effect. It was evident by an increase in speck count of the deinked pulp at high flotation pH.

The effect of chain length over the range C_{12} to C_{20} for linear saturated fatty acids is only minor. Addition of Ca^{2+} in the pulping stage at low levels of addition seems to improve the brightness response for deinking of newsprint with fatty acids. High levels of addition of Ca^{2+} seem to have a detrimental effect.

References

1. Woodward, T.W. - Proceedings of the Tappi Chemical Processing Aids Short Course, Tappi Press, Atlanta, p. 85, 1991
2. Larsson, A., Stenius, P. and Ödberg, L. - Svensk Papperstidning, 87(18): R158 (1984)

Chapter 6

Conclusions

Studies have been made on the effects of flotation conditions, feedstock composition, and surfactant during flotation deinking of newspaper (ONP) and magazine (OMG). It was found that flotation conditions, such as pH and temperature, feedstock composition, and surfactant have an important impact on deinking performance.

Sodium hydroxide addition in deinking is crucial. In the pulping stage, sodium hydroxide addition provides alkalinity which promotes swelling of fibres and breaking of interfibre bonds, which in turn facilitates loosening and detachment of ink particles from fibre surfaces. However, sodium hydroxide addition in deinking of wood-containing furnishes, such as newsprint, also promotes chromophore formation in the lignin, a phenomenon known as alkaline darkening, which leads to brightness loss of the deinked pulp. Addition of hydrogen peroxide, a common bleaching agent for mechanical pulp, can counterbalance the chromophore formation due to high alkalinity.

In the flotation stage, it was found that there is an optimum pH of 8.5 for flotation deinking of a 70/30 ONP/OMG furnish using a fatty acid type deinking surfactant. Higher pH leads to a loss of brightness. Chromophore formation due to high alkalinity still occurs in the flotation stage. It is important to note that the concentration of perhydroxyl anion (HOO^-), which is the active bleaching agent, is different in the pulping and flotation stage. Perhydroxyl anion concentration is lower in flotation stage due to dilution of the pulp stock or slurry prior to the flotation stage. However, it was found that the brightness loss at high pH in the flotation stage was

not only due to chromophore formation. It was also found that pH affects the performance of the surfactant in the flotation stage. The results of speck count analysis indicate that for the fatty acid type deinking surfactant used, there is an increase in the number of specks above pH 8.5. This suggests that re-deposition of ink particles onto the fibre is also contributing to the brightness loss in the flotation stage.

Increasing proportions of magazines (OMG), with ash content of 26%, in the waste paper feedstock results in a deinked pulp with higher brightness. Inclusion of OMG in deinking of ONP introduces inorganic fillers/coatings as well as bleached kraft pulp to the system. It was found that the higher brightness attained with increasing proportions of magazines (OMG) is largely due to the addition of higher brightness materials from the magazines, rather than a more efficient mechanism of ink removal from the ONP due to inorganic fillers/coatings.

Surfactant plays a significant role in deinking. In the pulping stage, the surfactant acts as a wetting agent and helps ink removal and dispersion. In the flotation stage, it promotes collection of ink particles onto air bubbles. The amount of surfactant added, pH, and temperature all affect the deinking performance of the surfactant.

In order to understand flotation deinking better, it helps to model the deinking process. Such a model can be divided into two stages, the pulping and flotation stages.

In the pulping stage, ink particles are detached from fibre and dispersed in solution. Surfactant in the pulping stage acts as a wetting agent which promotes more rapid penetration of chemicals into the fibre network and inter-fibre contact area and helps ink to break up and separate from the fibre. Surfactant molecules in the pulping stage can also act as emulsification/solubilisation agents, which help release the ink particles from the fibres and disperse them. It is important to note that the surfactant must be present at levels greater than the cmc for appreciable surfactant promoted

emulsification/solubilisation to occur, since it is the micelles which are responsible for emulsification/solubilisation. In emulsification/solubilisation, ink particles are enveloped in micelles with their hydrophobic ends facing the ink particles and hydrophilic ends directed toward water molecules. These enveloped ink particles appear hydrophilic, which helps them detached from the fibre and disperse in water. In addition to surfactant, high pH and temperature also helps loosen ink particles and subsequent ink detachment from the fibres.

In the flotation stage, which is carried out in a more dilute environment, the dispersed ink particles are deposited on air bubbles. When using fatty acid soaps, this is achieved by interaction of the hydrophilic ends of the soap molecules with calcium (Ca^{2+}) ions, which precipitates the soap as a layer of small particles on the surface of the much larger ink particles. This gives the ink particles the hydrophobic surface properties of calcium soap, which are expected to have a strong tendency to attach to the air bubbles. Excess calcium (Ca^{2+}) ion also can lower the charge on the ink particles, hence diminishing the repulsion between them and making them form small aggregates easily. Such aggregates will have a much better floatability than the individual ink particles.

Overdosing of surfactant in the flotation stage has a detrimental effect because excess surfactant is adsorbed onto ink particles, which make them appear hydrophilic, hence dispersing the ink particles and reducing their interaction with air bubbles. It is important to note that dilution of the concentration of surfactant occurs in the flotation stage.

Excessive calcium (Ca^{2+}) ion concentration in the pulping stage is not beneficial, since it impedes the dispersion of ink particles by forming ink particle aggregates which tend to be re-deposited onto the fibre surfaces.